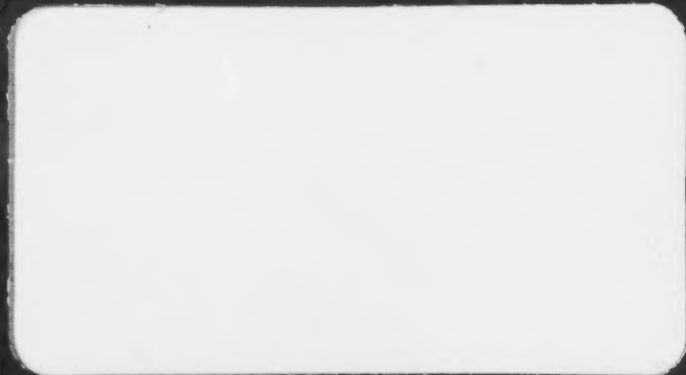




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PB 210 266

FINAL REPORT
DEVELOPMENT OF A FORMALDEHYDE ANALYZER
FOR
MOTOR VEHICLE EXHAUST EMISSIONS

PERIOD COVERED:
JULY 1, 1970 TO JUNE 30, 1971

CONTRACT NUMBER: CPA 70-170

PREPARED FOR
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
DURHAM, NORTH CAROLINA

AUTHORS: TIMOTHY H. JOHNSTON
ROLAND V. MARCOTE
RAMESH CHAND

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APPROVED: A. Eisenberg
S. EISENBERG, MANAGER
ENVIRONMENTAL PRODUCTS DIVISION

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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
2.0 DISCUSSION	2
2.1 Electrochemical Transducers	2
2.2 Sweep Voltammetry	5
2.2.1 Principles	5
2.2.2 Instrumentation	6
2.2.3 Experimental Procedure	9
3.0 EXPERIMENTAL RESULTS	10
3.1 Sweep Voltammetry Studies	10
3.1.1 Acidic Electrolytes	10
3.1.2 Basic and Neutral Solutions	17
3.1.3 Selected Electrolytes	22
3.2 Standard Formaldehyde Source	22
3.2.1 Evaluation of Various Sources	22
3.2.2 Characteristics of Formaldehyde Source	25
3.2.3 Wet Chemical Analysis of Formaldehyde	27
3.3 Evaluation of Membranes	31
3.3.1 Screening Studies	31
3.3.2 Development of Final Membrane	34
3.4 Evaluation of Electrolytes	36
3.4.1 Screening Test and Results	36
3.4.2 Discussion of the Results	38
3.4.3 Electrolyte-Exhaust Stream Compatibility Tests	40
3.5 Evaluation of Counter Electrodes	42
3.5.1 Screening Tests and Results	42
3.5.2 Compatibility and Fabrication Studies	44

TABLE OF CONTENTS - Continued

	<u>Page</u>
3.6 Evaluation of Sensor Electrodes	46
3.6.1 Platinum Electrodes	46
3.6.2 Gold Electrodes	50
3.6.3 Palladium and Rhodium Electrodes	50
3.6.4 Sensing Electrode-Exhaust Stream Compatibility Studies	51
3.7 Experimental Transducers	52
3.8 Selection of the Final Cell Configuration	53
4.0 PROTOTYPE CHARACTERIZATION	54
4.1 Interference Studies	54
4.1.1 Signal Interference	54
4.1.2 Physical Interference	58
4.2 Stability Studies	59
4.2.1 Span Stability	59
4.2.2 Zero Stability	59
4.2.3 Noise Level	59
4.3 Linearity	60
4.4 Temperature Effects	60
4.4.1 Signal Interference	60
4.4.2 Physical Interference	60
4.5 Life Time	63
4.6 Evaluation of Sampling Techniques	63
4.6.1 Redesign of Cell Sample Area	63
4.6.2 Ambient Sampling Conditions	64
4.6.3 Auto Exhaust Sampling Conditions	64

APPENDIXES

<u>APPENDIX</u>		<u>Page</u>
A	Instrument Operation and Design	66
B	Parts List	79

LIST OF FIGURES

<u>Figure No.</u>		<u>Page</u>
1	Electrochemical Transducer (Schematic)	3
2	Potentiostatic Control of An Electrochemical Transducer	4
3	Cyclic Voltammetric Instrumentation	7
4	Sweep Voltammetric Cell	8
5	Oxidation of Formaldehyde in 1.0 N Acetic Acid	11
6	Black Platinum Electrode Kinetics in 1.0 N H ₂ SO ₄	13
7	Oxidation of Formaldehyde in 1.0 N H ₂ SO ₄ , Platinum Electrode	14
8	Oxidation of Formaldehyde in 1.0 N H ₂ SO ₄ , Gold Electrode	14
9	Oxidation of NO ₂ , NO, and SO ₂ in 1.0 N H ₂ SO ₄ , Gold Electrode	16
10	Voltammogram of Formaldehyde in 10% NaOH	18
11	Voltammogram of Formaldehyde in 2% NaOH	19
12	Formaldehyde Oxidation in 10% K ₂ CO ₃	21
13	Oxidation of Formaldehyde in 10% K ₂ CO ₃ and 10% KHCO ₃	23
14	Formaldehyde Permeation Rate versus Temperature 15 cm Permeation Tube	28
15	Formaldehyde Permeation Tubes, Flow Rate versus Temperature	29
16	Formaldehyde Concentration versus Detection Current	61
17	Current Output versus Temperature	62

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Electrolyte Screening Study	37
2	Counter Electrode Screening Study	43
3	Effect of Pt Plating on Response Time	48
4	Chemical Treatment of Platinum Electrodes	49
5	Signal Interference Determinations, Exhaust Cell	56
6	Signal Interferences, Ambient Cell	57

1.0 INTRODUCTION

This is the final report summarizing the activities and results in the development of a formaldehyde analyzer for motor vehicle exhaust emissions. This work proceeded under the authority of the Environmental Protection Agency. The contractual designation was CPA 70-170.

The purpose of ~~this effort~~ was to develop an electrochemical transducer which would selectively oxidize formaldehyde in the midst of all of the other gas species present in the exhaust stream of internal combustion engines. The current generated by this device would be amplified and displayed in a manner which would permit quantitative analysis of the formaldehyde concentration.

The sensor which was developed was not as selective as proposed. However, its lack of selectivity applies only to members of the aldehyde family. It is equally sensitive to all aldehydes.

Development of the final sensor was accomplished by means of a thorough screening program in which hundreds of potential electrode-electrolyte-membrane combinations were evaluated and assessed for potential utility. The number of alternatives in the selection of the final configuration was severely limited by the fact that electro-oxidation was possible only in a basic electrolyte. Since this solution was not compatible with a severely acidic combustion environment certain compromises were made to effect a workable sensor. Basically, the sample was diluted and the sensitivity of the sensor was increased.

The problem of evaluating the sensor's performance necessitated the completion of two other significant achievements: 1. Production of a reliable formaldehyde standard in the 1ppm concentration range; and 2. Development of a wet method of analysis which would give accurate yet fairly rapid measurements at this low level of pollutant. The first requirement was satisfied by the creation of an alpha-polyoxymethylene permeation tube, the second by a unique application of the chromotropic acid method of analysis.

2.0 DISCUSSION

2.1 Electrochemical Transducers

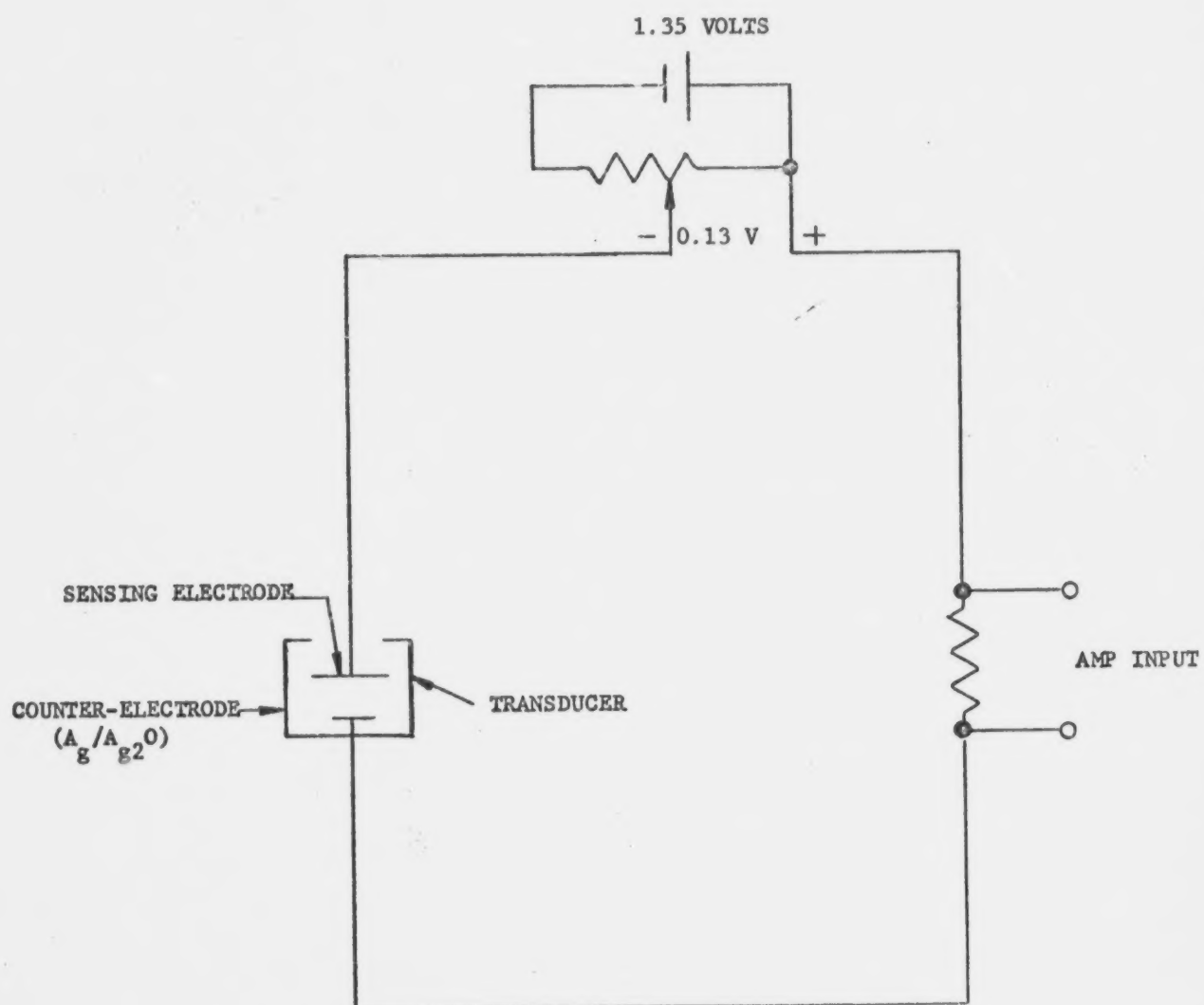
The heart of the formaldehyde detection system is the transducer; a self-contained, long-life, totally enclosed electrochemical cell. It is a current generating device in which the absorbed gas molecules are oxidized at a sensing electrode. The current which is produced is directly proportional to the partial pressure of the gas in the mixture under analysis.

A simplified schematic of an electrochemical transducer is depicted in Figure 1. The formaldehyde molecules diffuse through the protective semipermeable membrane into the thin film of electrolyte. The dissolved species then diffuse to the sensing electrode where they undergo electro-oxidation. Since the rate of response is dependent on the rate of diffusion through these two mediums, it is necessary to keep the total thickness to a minimum.

The sensing electrode is connected externally through the bias network depicted in Figure 2 to the counter electrode. The counter electrode material usually has a higher oxidation potential than the pollutant. The sensing electrode is a polarizable electrode which assumes a selective potential maintained by the counter electrode and adjusted through the use of a stable D.C. power source. A mercury battery is used so that the potential remains constant when the instrument power is off. The pollutant molecules upon reaching the sensing electrode encounter a potential higher than that required for their oxidation. Electrochemically, while the pollutant is being oxidized at the sensing electrode, a corresponding reduction reaction occurs at the counter electrode. The resulting current is diffusion limited and is a function of the concentration gradient between the membrane and the sensing electrode. Since this gradient is directly proportional to the partial pressure of the formaldehyde in the sample (a relationship derived through Fick's Law of Diffusion), the oxidation current is directly proportional to the formaldehyde concentration. Thus we are able to express the formaldehyde concentration by

FIGURE 2.

SCHEMATIC SHOWING POTENTIOSTATIC CONTROL OF
ELECTROCHEMICAL TRANSDUCER TO OBTAIN CH₂O SELECTIVITY



measuring the generated current. The diffusion current is expressed by the equation:

$$i = \frac{nFADC}{\delta}$$

Where i is the current in amps, n is the number of exchanged electrons per mole of pollutant, F is the Faraday constant (96,500 coulombs), D is the diffusion coefficient of the gas in $\text{cm}^2/\text{sec.}$, C is the concentration of the formaldehyde in the sample and δ is the thickness of the diffusion layer.

2.2 Sweep Voltammetry

2.2.1 Principles

The use of sweep voltammetry as a tool in selecting the most promising candidate electrolytes has been adopted as standard procedure in this laboratory for sometime. The technique permits the scanning of an entire voltage range in a matter of minutes. The same process with an experimental transducer would take days. The resultant scan is a record of the current changes, due to electrochemical reactions at the sensing electrode, as a function of the potential of the electrode.

In the evaluation of sweep voltammograms the most useful parameters are the potentials at which oxidations or reductions occur and the rate of current change.

The approximate potential of an reduction or oxidation reaction is determined at the maximum current value for that reaction. This is usually the value at the apex of a peak, which is referred to in the text of this report as the peak potential. This current peak results from a localized depletion of the reacting species at the electrode site and is not to be confused with a discontinuance of the reaction at ensuing potentials. For an oxidation reaction the peak is a good indication of the minimum potential which must be used to achieve efficient oxidation. In the case of a reduction it represents the maximum potential which can be applied before the reduction process becomes inefficient. The value of the peak potential is a function of the scan rate. In comparison analysis this

parameter should be kept constant.

The efficiency and rate of a reaction can be evaluated by the shape of the reaction curve. An efficient reaction is characterized by a peak as opposed to a plateau or continuous slope. A fast reaction rate is indicated by a sharp peak. A slow reaction is characterized by a broad hump.

Sweep voltammetry is also useful in evaluating electrode kinetics and the compatibility of the electrode-electrolyte couple. Sweep voltammetry was utilized during this contract to find an electrolyte which showed selective oxidation for formaldehyde and which displayed the properties of an efficient oxidation medium.

2.2.2 Instrumentation

A schematic of the instrumentation package assembled for cyclic voltammetric measurements is shown in Figure 3. A potentiostat maintains the voltage between the reference electrode and the working electrode at a value equal to the sum of the DC reference and function generator voltages. The potentiostat accomplishes this by controlling the current between the working and counter electrodes. It senses the difference between the reference and working electrode voltages and compares it to the reference input voltages by means of a high gain amplifier system. The output is fed through the working electrode-counter electrode pair. The system permits the measurement of current-voltage-time relationships under well-defined conditions. No voltage change is possible at the reference electrode. Thus, the measurements reflect only the voltage changes at the working electrode-electrolyte interface, independent of ohmic losses through the electrolyte and polarization at the counter electrode.

Voltage sweep measurements are made in a two compartment cell with three electrodes (Figure 4). The reference chamber contains the reference electrode and is connected to the main compartment via a small capillary which acts as the

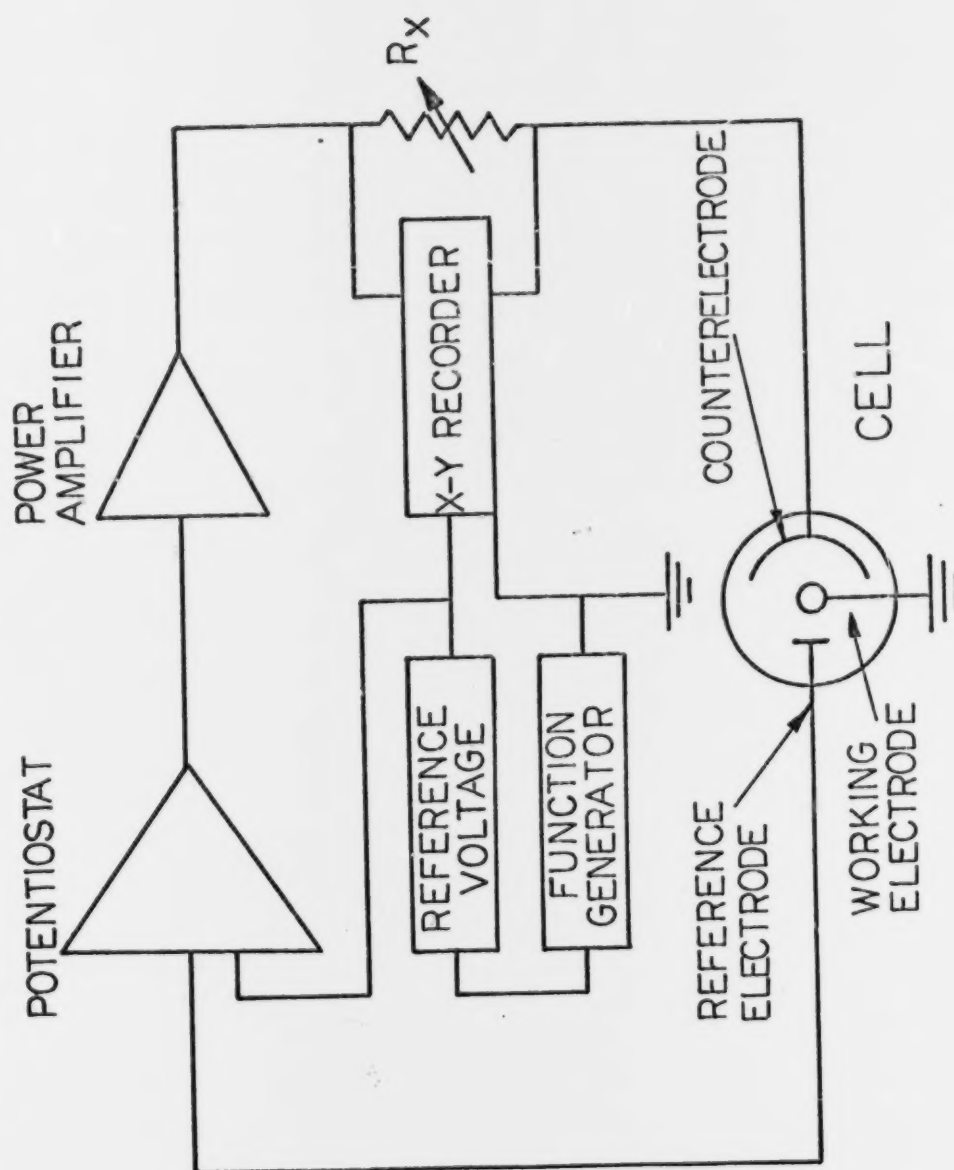


FIGURE 3. CYCLIC VOLTAMMETRIC INSTRUMENTATION

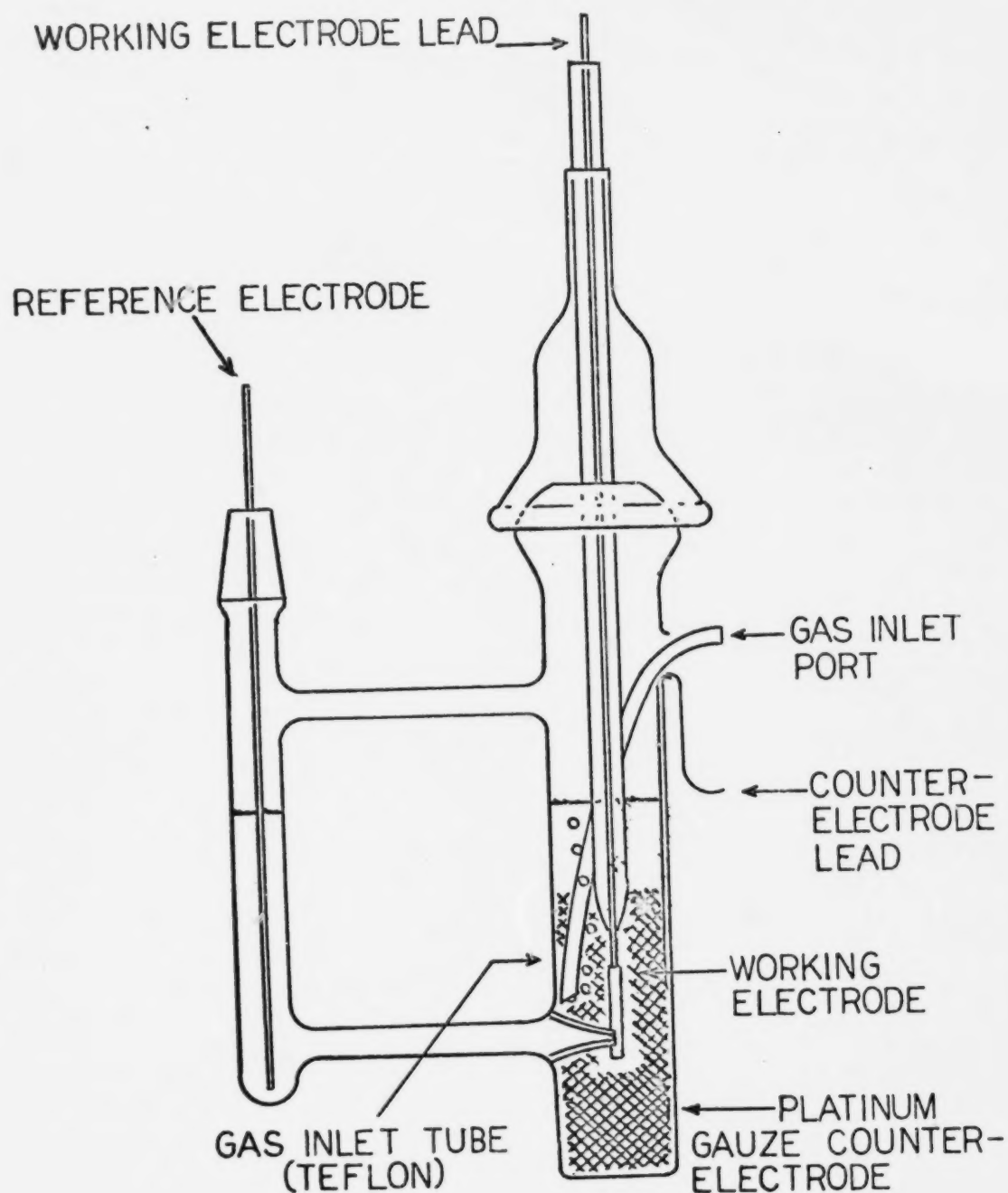


FIGURE 4. SWEEP VOLTAMMETRIC CELL

electrolyte bridge. For most electrolytes a saturated calomel reference electrode is satisfactory. The working electrode and counter electrode are situated in the main compartment. The working electrode is usually a noble metal such as a gold or platinum since the same material would be used as the sensing electrode in the final transducer. The dimensions are held constant at 1.0 x 0.3 cm for ease of comparison between different materials. The tip of the Luggin capillary is notched in a vertical direction to allow reproducible positioning of the working electrode. The working electrode is totally enclosed by a platinum counter electrode to ensure an omnidirectional charge distribution. Both compartments of the cell are filled with the same electrolyte.

2.2.3 Experimental Procedure

The sweep voltammetry cell is initially washed with an industrial detergent, rinsed with distilled water, immersed in 50% HNO_3 acid, and cleaned again with distilled water. It is then rinsed with the electrolyte to be used in the experiment and filled with electrolyte. Normally, for subsequent determinations, the cell need only be rinsed with distilled water and treated with the electrolyte to be investigated.

The working electrodes are cleaned in hot 50% aqueous HNO_3 , rinsed with water, immersed in hot 45% aqueous KOH , rinsed with water, and washed finally with the electrolyte.

The reference electrode is washed with distilled water and electrolyte before use. The platinum counter electrode is flame annealed and then rinsed.

In the process of generating sweep curves the first step is usually to record the background current for the plain electrolyte. Next, known amounts of the molecule to be studied are added either as a solid or a gas. The solution is then aerated with nitrogen to get rid of all traces of oxygen. The nitrogen flow is stopped and the sweep curve is recorded.

3.0 EXPERIMENTAL RESULTS

3.1 Sweep Voltammetry Studies

Many sweep curves were made to evaluate the feasibility of rapid, selective oxidation of formaldehyde. The shape of the various curves allowed us to predict which electrolytes would be most promising for the rapid detection of formaldehyde. The potentials of the reactions allowed us to select those electrolytes which would permit selective oxidation of formaldehyde. Background traces were used to determine possible interference from the electrolyte itself.

Determinations were made with gold and platinum electrodes to determine the relative value of each. All curves were made at a sweep rate of 50 seconds per cycle. Voltammograms were also made of O_2 and NO_2 containing solutions since these two exhaust stream components, by themselves, would most likely determine the potential at which selective oxidation of formaldehyde would have to take place. A brief explanation of this statement should suffice. Oxygen has a definite reduction potential which cannot be eliminated. Thus all determinations must be made above this potential. Nitrogen dioxide is usually both reduced and oxidized over a very narrow potential range. The transition potential or plateau between the oxidation and reduction is usually the only voltage where selective oxidation can be recorded unless the NO_2 can be scrubbed from the sample. With formaldehyde this option was not available because the chemical reactivity of the molecule prohibits the presence of any type of scrubber in the sampling system.

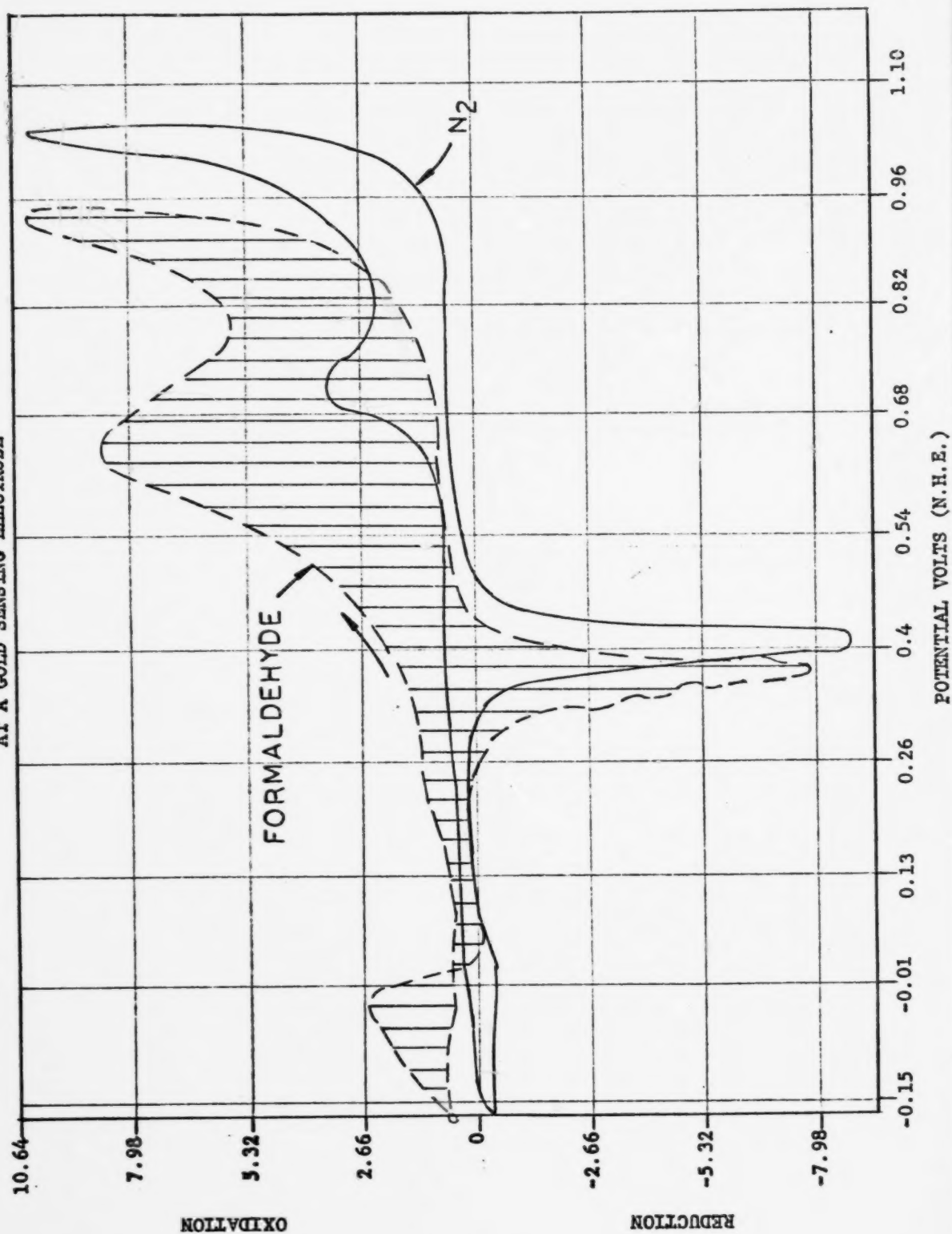
3.1.1 Acidic Electrolytes

The initial supporting solutions studied were acids.

a.) Aqueous organic acids - Typical curves for the 1.0 N acetic acid system are shown in Figure 5. The solid curve shows the oxidation-reduction reactions of 1.0 N acetic acid at a gold electrode after treatment with nitrogen. At 0.4 V acetic acid is reduced to ethanol.

At 0.65 V it is oxidized to acetaldehyde. The upper limiting potential

FIGURE 5
OXIDATION OF FORMALDEHYDE IN 1.0 N ACETIC ACID
AT A GOLD SENSING ELECTRODE



in this medium is 0.88 V, a value well below the potential of the most commonly used counter electrode. As can be seen by the broken line curve the formaldehyde oxidation overlaps the acetic acid at +0.6 V. Since the formaldehyde concentration in the curve is 1000 times larger than the concentrations found in the sensor it can be seen that if acetic acid were employed in the transducer an abnormally high and unstable background current would make the detection of formaldehyde difficult. Electrolytes composed of 1.0 N formic acid and 1.0 N butyric acid gave very similar results. It is apparent that most partially oxidized organic molecules are electrochemically active in the 0.4 to 0.8 potential range in an aqueous acidic medium. This property makes the use of aqueous organic electrolytes as a sensing medium impractical.

b. Sulfuric Acid

1.) Platinum sensing electrode - It was reported by Buck and Griffith⁽¹⁾ that the reproducibility of the black platinum electrode in electrochemical applications was seriously impeded by the formation of platinum oxides. For sweep voltammetry evaluations this property was not an obvious impairment. A sweep of 1.0 N H₂SO₄ at a platinum electrode after treatment with nitrogen is presented in Figure 6. The oxidation of platinum commences at 0.75 V. Reduction of the platinum oxides occurs at 0.72 V. Absorbed hydrogen peaks can be plainly seen at the lower potentials, 0.1 - 0.3 V. The sensitivity for this curve was 100 times greater than normal.

The curve for formaldehyde at a platinum electrode is shown in Figure 7. The primary oxidation peak occurs at 0.89 V during the positive sweep. The positive peak which appears during the negative sweep

(1) Journal of the Electrochemical Society, Nov. 1962 - p. 1005.

FIGURE 6
BLACK PLATINUM ELECTRODE KINETICS IN 1.0 N H_2SO_4

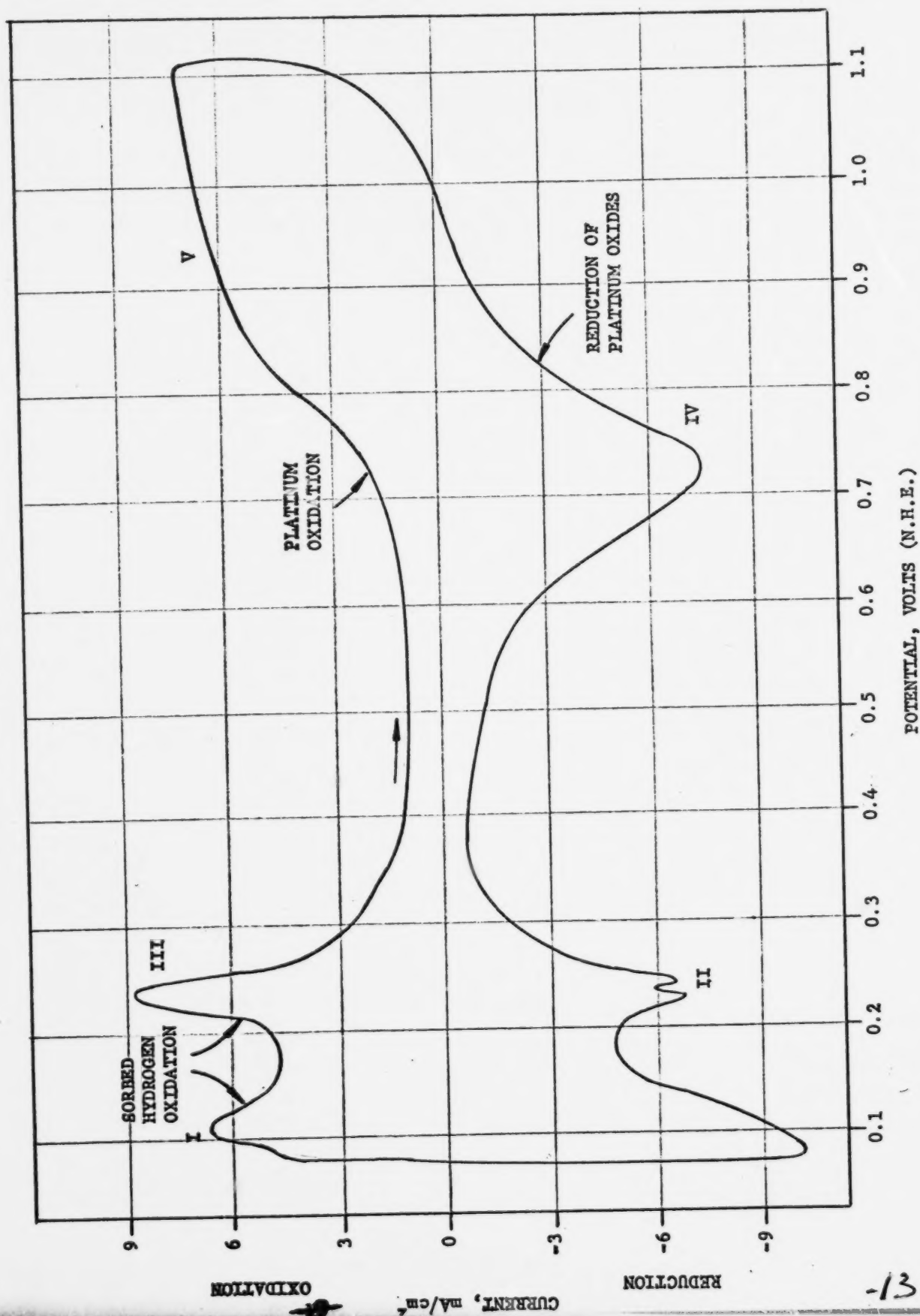


FIGURE 7

OXIDATION OF FORMALDEHYDE IN 1.0 N H_2SO_4 AT A PLATINUM SENSING ELECTRODE

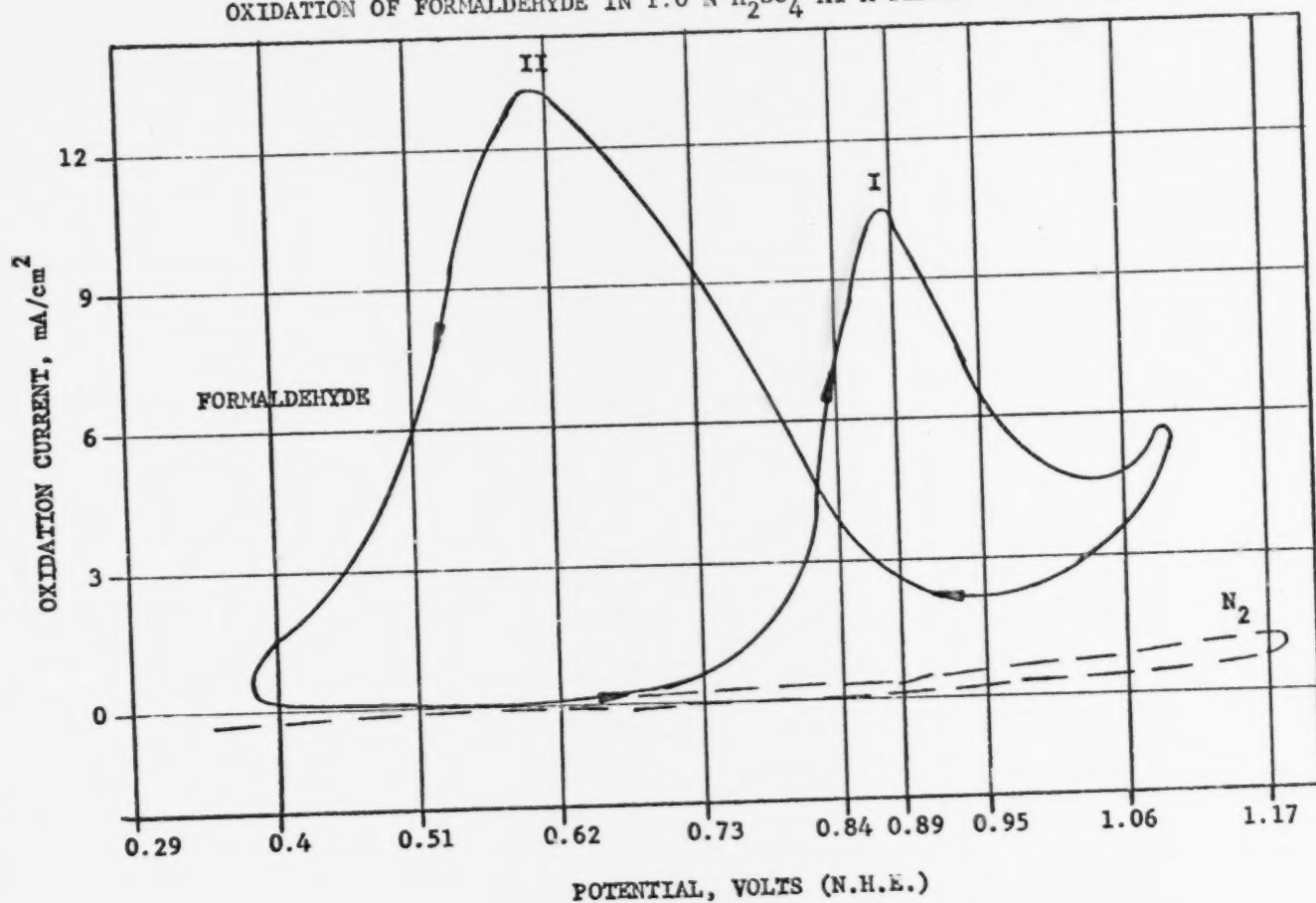
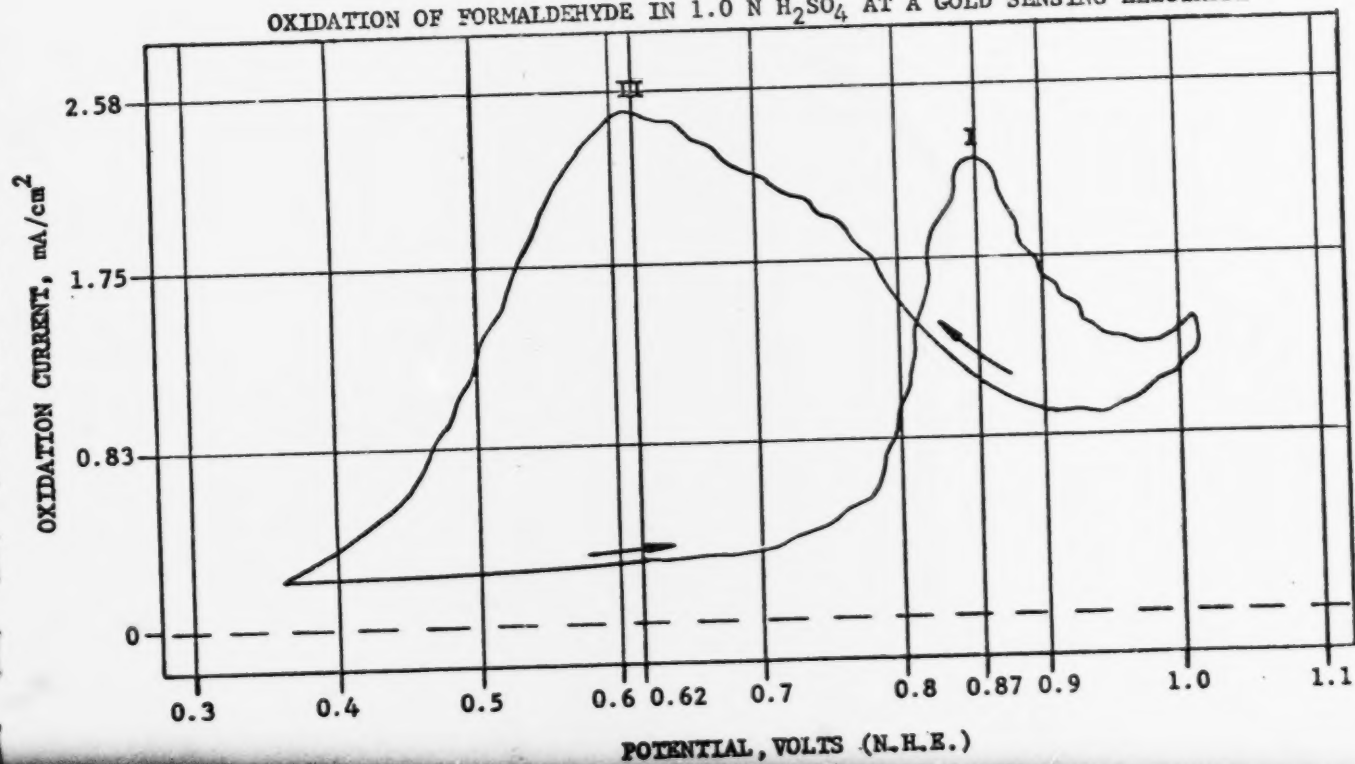


FIGURE 8

OXIDATION OF FORMALDEHYDE IN 1.0 N H_2SO_4 AT A GOLD SENSING ELECTRODE



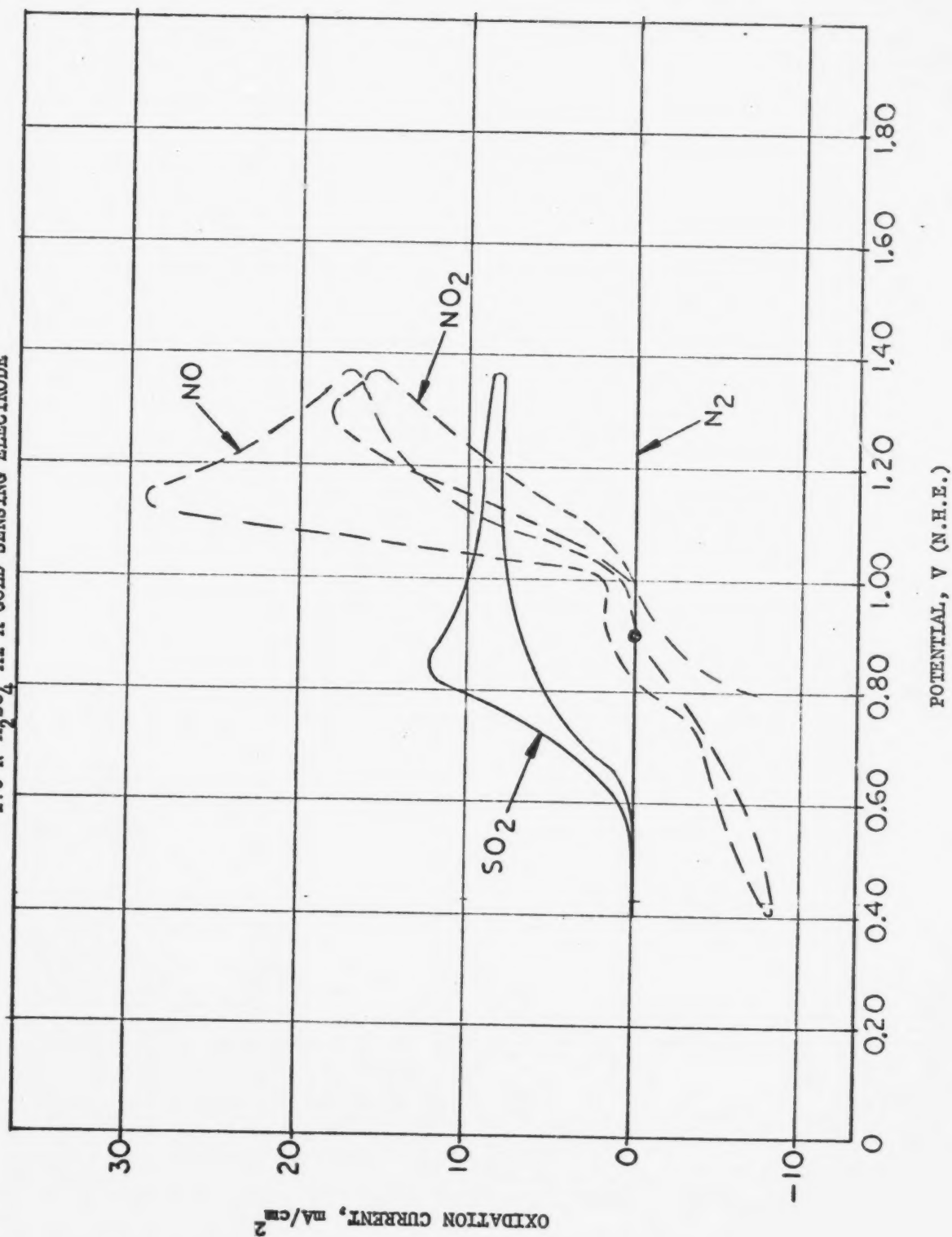
is not part of the oxidation sequence of formaldehyde. It is an anomaly which was observed throughout the sweep studies. Its potential was found to be independent of pH and solute species. Its disappearance was observed only in hydroxyl bases.

The oxidation peak at 0.89 V was sharp enough to be indicative of a fast reaction. However, the oxidation potential was about the same as carbon monoxide. Unless a highly selective membrane could be found this interference would make the use of a platinum electrode impractical.

2.) Gold Sensing Electrode - A potential sweep of a formaldehyde solution in 1.0 N H_2SO_4 with a gold electrode yielded a curve (Figure 8) very similar to that obtained with platinum. The gold electrode was not as efficient however. The area under the oxidation peak was four times smaller than platinum. It should be noted that the electrode system for the detection of formaldehyde must be very efficient. The absorption factor for formaldehyde in most aqueous solvent systems is 100%. If all of the absorbed formaldehyde is not immediately oxidized at the sensing electrode, the system will be non-linear and plagued by very slow recovery rates. The gold electrode was superior to platinum in that interference from carbon monoxide was not as great a problem.

Interference from NO and NO_2 would not be a problem either as evidenced in Figure 9, but it was certain that in instances where SO_2 was contained in the gas stream a gross interference would be confronted.

FIGURE 9
 OXIDATION OF NO_2 , NO AND SO_2 IN
 1.0 N H_2SO_4 AT A GOLD SENSING ELECTRODE



3.1.2 Basic and Neutral Solutions

- a.) 10% Aqueous Sodium Hydroxide - Formaldehyde exhibits one oxidation peak with a gold electrode at -0.172 V in 10% NaOH (Figure 10). The peak at +0.1 V is not due to formate oxidation. Later studies with sodium hydroxide and sodium formate did not reveal any substantial formate oxidation peaks in this region. The formate reduction which starts at -0.55V was verified with a formate solution. It was also observed that the reduction did not occur until after a formaldehyde oxidation sweep was made. A voltage sweep of oxygen in this electrolyte revealed that a lower limiting potential of +0.1 V would prevent oxygen interference in the detection of formaldehyde.
- b.) 2% NaOH plus 0.5 N Sodium Formate - Sweep voltametric studies of this electrolyte using a gold electrode, Figure 11, revealed that formate oxidation or reduction peaks are absent in the potential range -0.45V to +0.5V. The oxidation of formaldehyde in this electrolyte occurs at -0.188V. The oxygen reduction wave begins at +0.1V.
- c.) 10% Aqueous Potassium Carbonate - Investigation of formaldehyde oxidation in carbonate and bicarbonate mediums was undertaken because of the anticipated incompatibility of a hydroxide medium with the CO₂ in the gas stream. Carbonate and bicarbonate solutions derive their basicity from disassociation equilibriums due to the weak acidity of carbonic acid.



The possibility that the carbonate and bicarbonate mediums would be neutralized by CO₂ was considered to be unlikely, or at the worst, minimal.

FIGURE 10
VOLTAMMOGRAM OF CH_2O , N_2 AND
 O_2 IN 10% NaOH
AT A GOLD ELECTRODE

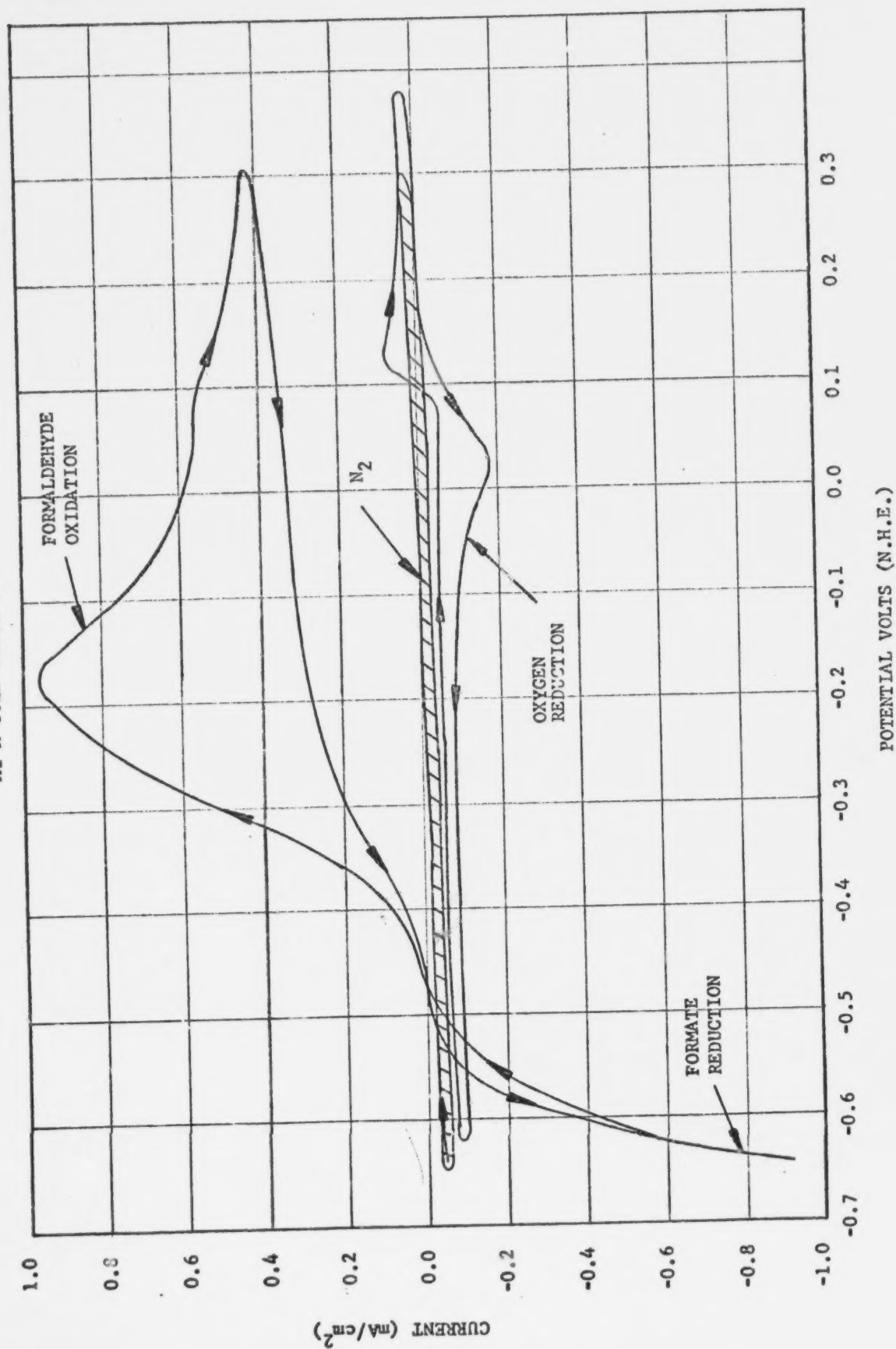
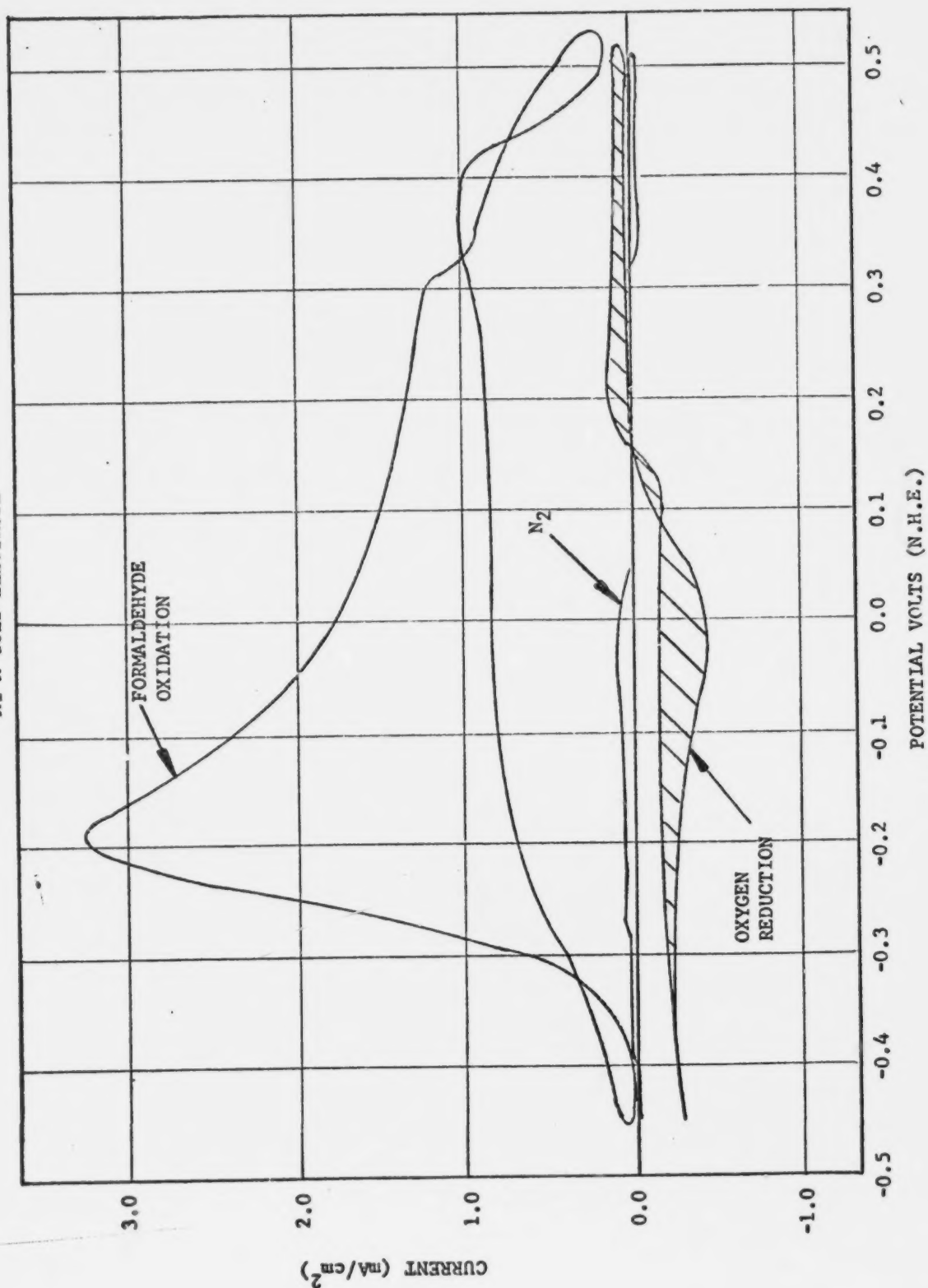


FIGURE 11

VOLTAMMOGRAM OF CH_2O , O_2 and N_2 IN
0.5N FORMATE + 2% NaOH
AT A GOLD ELECTRODE

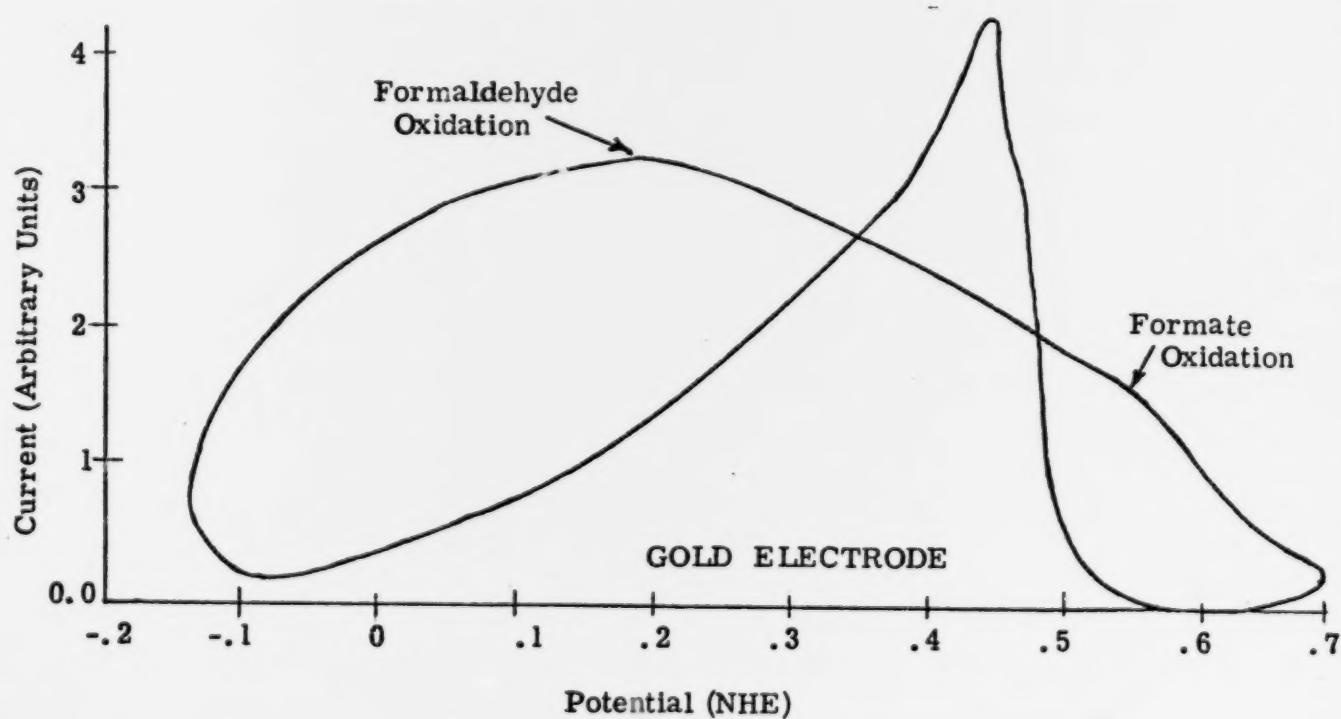
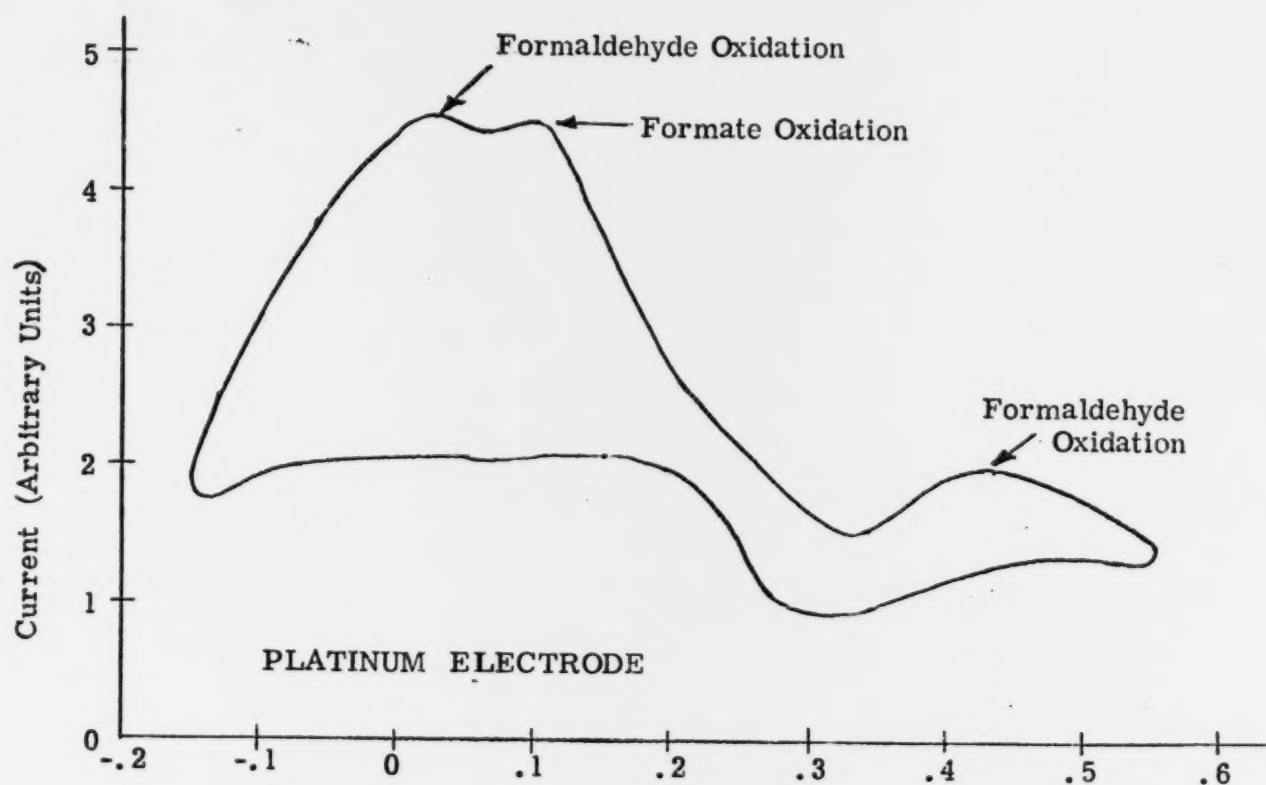


Voltammograms of formaldehyde oxidation in these two solutions were made with gold and platinum electrodes (Figure 12). The formaldehyde oxidation curve for gold is broad with a gentle slope indicating a slow reaction. The curve for platinum is quite the opposite. The peak at 0.001 V is fairly sharp. In addition, an oxidation peak occurs at 0.4V. This is most likely an overvoltage catalyzed oxidation which would be fairly fast. The negative sweep oxidation peak was missing with platinum but was conspicuously present with gold. This was not expected since the pH of the carbonate solution was greater than 11. The only difference between the carbonate and the sodium hydroxide electrolytes was the indirect origin of the hydroxide ion. The sensitivity of 10% K_2CO_3 to formaldehyde was sufficient enough to warrant further investigation. Reduction of O_2 did not occur above +0.2V and a plateau at +0.45V was observed between the oxidation and reduction of NO_2 . Selective oxidation of formaldehyde in a carbonate media would most likely take place at this potential.

d.) 50% Aqueous Potassium Carbonate.- The pH of this solution was slightly greater than 12. A potential shift of -0.2 V was observed from the voltages obtained with 10% K_2CO_3 . The slope and magnitude of the peaks were roughly equivalent.

e.) 10% Potassium Bicarbonate - Oxidation of formaldehyde in 10% bicarbonate at a gold electrode was a very slow reaction. The hump was so broad that a peak as such was not clearly defined. At a platinum electrode the reaction appeared to be more reversible. The primary oxidation peak was at .225V, the secondary peak was at 0.68V. The shape of the curve was almost identical to that obtained in 10% K_2CO_3 .

Figure 12. Formaldehyde Oxidation in 10% K_2CO_3



f.) 10% Potassium Bicarbonate plus 10% Potassium Carbonate - Sweep curves obtained in this mixture at a gold electrode were for some reason much better than those obtained in the individual solutions (Figure 13). The primary oxidation peak was at 0.6V. The peak, although sharper than those obtained in K_2CO_3 or $KHCO_3$ still did not have the properties associated with a rapid reaction.

g.) 1N Potassium Chloride - Sweeps conducted in this neutral electrolyte did not reveal any distinguishable oxidation or reduction peaks.

3.1.3 Selected Electrolytes

The most promising electrolyte-sensing electrode combinations as determined by sweep voltammetry were:

- a.) Platinum Electrode - 1N H_2SO_4
- b.) Gold Electrode - 10% KOH
- c.) Platinum Electrode - 10% K_2CO_3
- d.) Platinum Electrode - 10% $KHCO_3$

Platinum was selected with H_2SO_4 because of its efficiency. Potassium hydroxide was selected in lieu of sodium hydroxide because of its greater solubility.

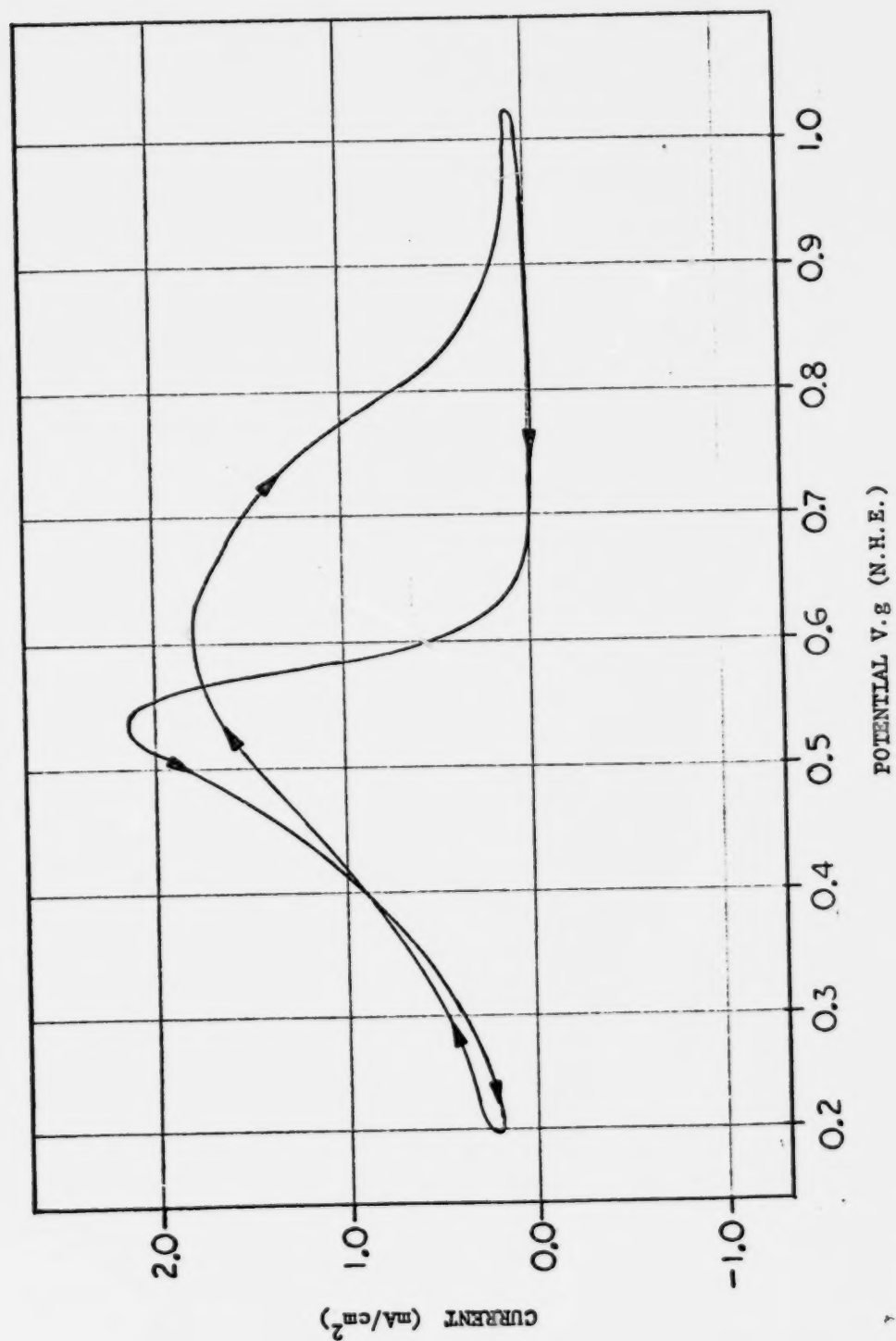
3.2 Standard Formaldehyde Source

3.2.1 Evaluation of Various Sources

Pure, dry formaldehyde is stable only at temperatures of 80 to 100°C. At ordinary temperatures the dry gas polymerizes slowly depositing a white film of polyoxymethylene. This polymerization reaction is best described as a polymolecular surface reaction at pressures lower than 200 mm. It must also be noted that the polymerization process is strongly catalyzed by trace amounts of water.

The analytical properties of a formaldehyde detector could not be evaluated without the use of a dependable formaldehyde source. Thus, in the course of this study it was necessary to prepare formaldehyde gas streams of known concentrations.

FIGURE 13
OXIDATION OF FORMALDEHYDE IN
10% KHCO_3 + 10% K_2CO_3
AT A GOLD ELECTRODE



The possibility of preparing standards by passing nitrogen over or through a formaldehyde solution (13% methanol) was evaluated. This source of formaldehyde was found, as previously reported, unsuitable. The main drawback was the methanol interference on the selective sensing of formaldehyde.

A second method was based on the generation of a CH_2O pressure by heating paraformaldehyde ($\text{P}-(\text{CH}_2\text{O})_n$) to 120°C in a stainless steel tank. The liberated formaldehyde was then transferred to another heated stainless steel tank which had been evacuated. Once the desired CH_2O pressure was obtained, the tank was pressurized to 1500 pounds with nitrogen.

Various difficulties were encountered in the preparation of CH_2O gas streams by this method. The results obtained were not consistent indicating the possibility of polymerization.

Another of the methods investigated consisted of passing dry nitrogen over permeation tubes maintained at constant temperature. Initial tests on permeation tubes involved the use of paraformaldehyde. A reproducible formaldehyde standard could not be obtained from paraformaldehyde for two important reasons:

1. Paraformaldehyde has a water content of 2 to 4% even after desiccation. This high amount of water caused the polymerization of formaldehyde in the gas stream.
2. The structure of paraformaldehyde is characterized by low molecular weight oligomers, which lend amorphous random properties to the crystalline state.

The partial pressure of paraformaldehyde and other polymeric forms of formaldehyde is due to "unzippering" depolymerization reactions at the hydroxyl end groups. The rate of thermal decomposition is accordingly dependent on the number and availability of end groups. The attainment of equilibrium partial pressure is extremely difficult with a polymer such as paraformaldehyde since it is characterized by widely varying chain lengths and ill-defined solid state surface structures.

Accordingly a search was made for a polymer characterized by uniform chain lengths, a high degree of polymerization, a well defined crystalline structure, and low water content. These properties were found in alpha-polyoxymethylene. Properly prepared, it typically has a formaldehyde content of 99.7 to 99.9%. The degree of polymerization is believed to be an average chain length of 200.

The alpha-polyoxymethylene was prepared by adding potassium hydroxide to 40% methanol-free aqueous formaldehyde solution. The KOH pellets were slowly added until a 1 KOH/500 CH₂O molar ratio was reached. The alpha-polyoxymethylene so obtained was vacuum filtered, washed with ethanol and ether, and stored in a desiccator. The operation was repeated twice at KOH/CH₂O molar ratios of 1:100 and 1:20.

The equilibrium pressures have already been well-defined in the range 80 to 100°C by Iwasa and Imoto⁽²⁾. These pressures follow the equation:

$$\log P_e = 12.02 - 3.37 \frac{10^3}{T^\circ}$$

where P_e is the CH₂O partial pressure and T° is temperature.

Permeation tubes were constructed with 15 cm lengths of 1/4" commercial teflon tubing with a wall thickness of 0.03 inches. The tubes were filled with alpha-polyoxymethylene. The ends were closed with teflon plugs and clamped shut. Tests were conducted at temperatures of 100 and 130°C. The gas stream was nitrogen used at a flow rate of 1.0 SCFH. Calculations of the permeation rates were made via weight loss measurements every 24 hours at 100 and 130°C. A gas stream containing 97 ppm H₂CO was obtained at 130°C with a variance of ±2%. At 100°C a concentration of 11.5 ppm was obtained. Tests with a 10 cm length of 1/8" tubing at 100°C yielded a gas stream containing 1.0 ppm H₂CO.

3.2.2 Characteristics of Formaldehyde Source

A test program was set up to establish the reliability of the alpha-polyoxymethylene permeation tubes.

Permeation tubes containing alpha-polyoxymethylene were prepared by a standard method for the evaluation. All of the tubes were identical in configuration. They were prepared from 1/4" O.D. commercial teflon tubing with a wall thickness of 0.03". They were designed to have a sample chamber exactly 15 cm long. A typical tube contained 1.2 grams of alpha-polyoxymethylene.

Tests were conducted to characterize the following four properties of the tubes:

1. Variation in permeation rates from tube to tube.
2. Stability of the permeation rates of selected tubes for one week at temperatures of 100°C and 130°C.
3. Variation in permeation rate with respect to flow rate.
4. Variation of permeation rate with respect to temperature. Except where noted tests were conducted with dry nitrogen at a flow rate of 1.0 SCFH at 130°C.

Variation in the permeation rate between different tubes was found to be $\pm 7\%$ with respect to the arithmetical mean. This deviation is attributed to the physical properties of the tubing since the vapor pressure of alpha-polyoxymethylene is well characterized in this temperature region.

The permeation rate stability was determined individually for three tubes. The rates were found to be constant within $\pm 2\%$ for each of the tested tubes at both 100 and 130°C. This variation was decreased to $\pm 0.5\%$ by placing a stainless steel coil in front of each of the tubes to minimize the effect of the carrier gas temperature. During this test it was determined that each permeation tube has a life expectancy of 12-14 days when used continuously at 130°C and 6-8 months at 100°C.

By varying the dry nitrogen flow rate from 0.5 to 5 SCFH it was demonstrated that the permeation rate in this flow range is independent of the rate of removal of formaldehyde from the surface of the permeation tube.

Permeation rates do vary with temperature and the properties of the teflon tubing. Thus it is necessary to calibrate each tube in order to obtain accurate formaldehyde concentrations. A typical weight-loss temperature curve is presented in Figure 14. A complete calibration curve is outlined in Figure 15. Since the permeation rate is not a function of the carrier's flow rate, a single point calibration may be sufficient for a tube which is to be used to supply formaldehyde over a narrow concentration range.

3.2.3 Wet Chemical Analysis of Formaldehyde

Evaluation of the permeation characteristics of the permeation tubes was achieved primarily through the use of weight loss techniques. At the lower concentration levels this method was not always reliable. Weight losses were often less than 1 mg/day and the weights obtained were accurate only within 0.2 mg. For this reason an effective wet chemical method for the direct determination of formaldehyde from low concentration gas streams was developed.

The spectrophotometric analysis developed for this purpose was based on the reaction of chromotropic acid with formaldehyde.

The normal procedure for employing this method is to remove the formaldehyde from the gas stream with a sintered glass gas scrubber filled with water. This method has many drawbacks, chief among them being the following:

- 1.) Water-filled scrubbers are inefficient, absorbing only 70-75%. addition of a basic medium increases the efficiency somewhat but it interferes with the subsequent analysis which takes place in a strongly acidic solution.
- 2.) Final analysis of the scrubbed sample requires at least a 50 to 1 dilution. This increases the size requirements of the sample tremendously.

FIGURE 14

FORMALDEHYDE PERMEATION RATE
VERSUS TEMPERATURE
15 CM PERMEATION TUBE

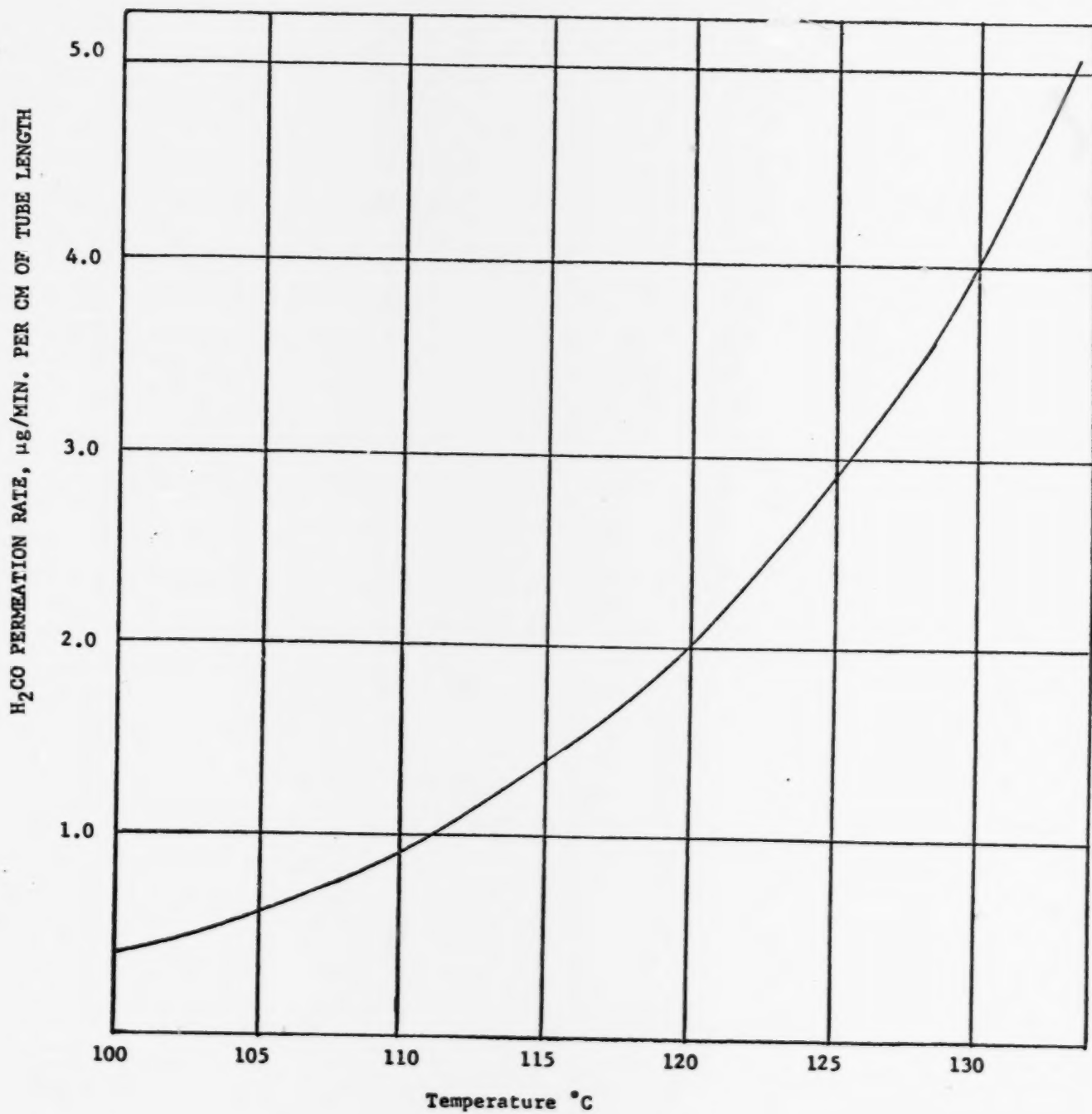
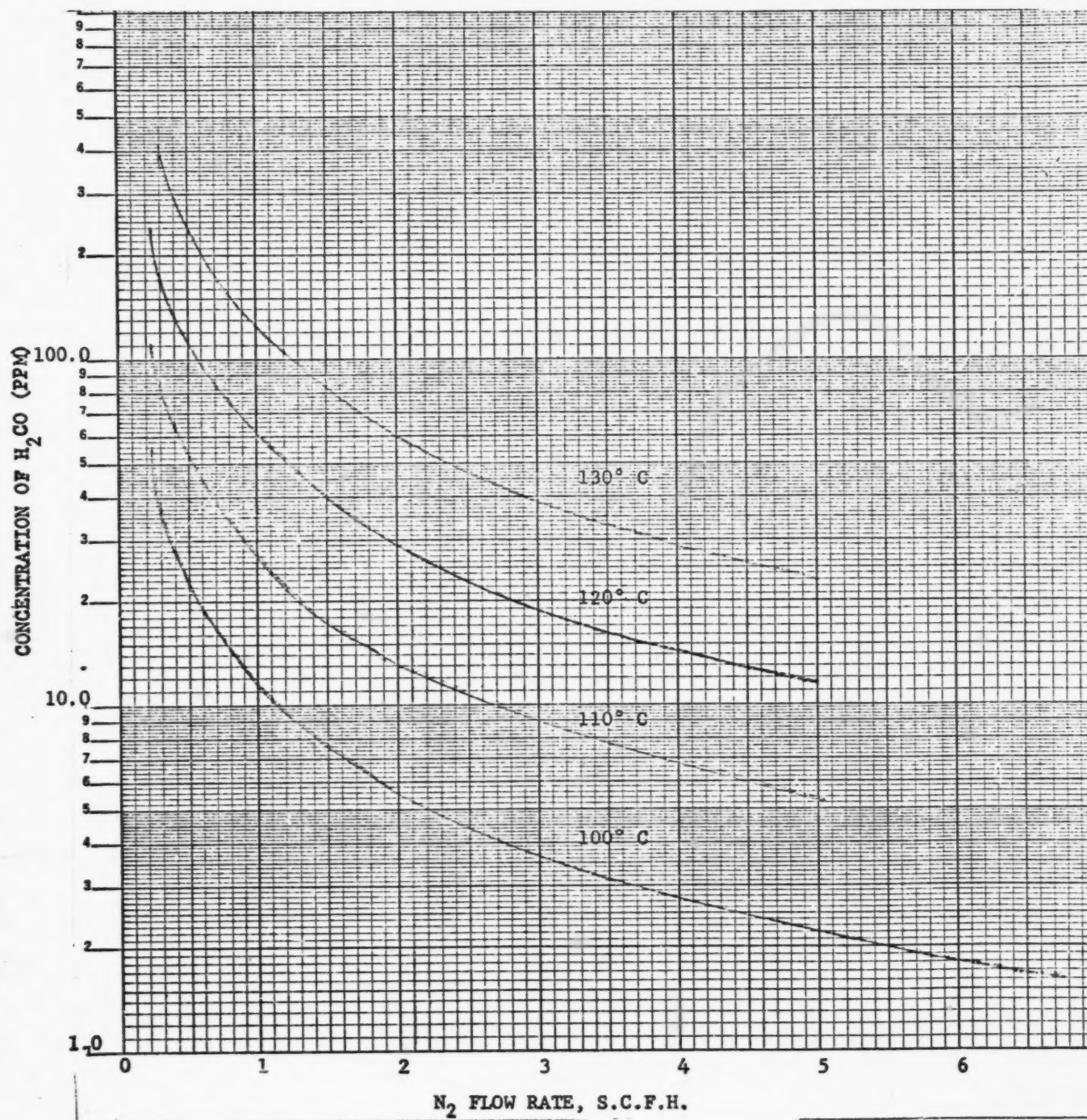


FIGURE 15
FORMALDEHYDE PERMEATION TUBES
FLOW RATE VERSUS CONCENTRATION



An innovative method of analysis was evolved and substituted to eliminate these problems. The chromotropic acid is dissolved directly in concentrated sulfuric acid. The scrubber is filled with this solution. A 125 ml scrubber with 35 ml of solution was found to be adequate.

Concentrated H_2SO_4 is very viscous and has a high surface tension. As the gas stream bubbles through, a foam of bubbles 2-3" thick forms on top of the mixture. This increases the scrubbing efficiency to almost 100%. (A second scrubber placed in series with the first was found to be void of formaldehyde.) The scrubber solution is washed into a 50 ml volumetric and the color development is made directly on this sample without dilution. Results were found to have very little variance. Linearity of the standards was perfect over the range tested. The complete procedure is given in detail below.

Reagents:

Chromotropic Acid: Dissolve 1g chromotropic acid in 500 ml concentrated H_2SO_4 with heat and magnetic stirring. Dilute to 1000 ml with concentrated H_2SO_4 .

Standard: Dissolve 100 mg. alpha-polyoxymethylene in 100 ml concentrated H_2SO_4 . Dilute 5-100 with concentrated H_2SO_4 . This is the standard stock solution.

Sample Preparation: Place 35 ml of sample solution in a 125 ml scrubber. Bubble the sample through to get 25 μ g of formaldehyde. For a 2 ppm gas stream this takes about 18 minutes. Wash the solution into a 50 ml volumetric and bring to volume.

Analysis Procedure:

- 1.) Dilute the standard stock solution 1:100 and 2:100 with chromotropic acid.
- 2.) Heat equal portions of a chromotropic acid reagent blank, the sample, and the standards for 20 minutes in boiling water.

3.) Cool and read the absorption at 570 mμ with a colorimeter or Beckman D.U.

4.) Construct a standard curve and extract the concentration of the sample simply as total grams formaldehyde in the sample.

5.) Calculations:

$$\text{Gas Stream Conc. (PPM)} = \frac{\text{CH}_2\text{O in sample (g)} \times 10^6}{\text{Flow rate } \frac{1}{\text{hr}} \times \frac{1\text{M}}{22.4 \text{ l}} \times \frac{30\text{g}}{\text{m}} \times \text{Time (hr.)}}$$

Agreement between this method of analysis and the weight loss method was exceptionally good. The direct method usually ran 4% lower than the weight loss method at small concentrations.

3.3 Evaluation of Membranes

3.3.1 Screening Studies

The membrane is an integral part of the electrochemical transducer. Although its most important property is the permeability of the gas to be analyzed, it has many other important functions. It must: contain the electrolyte reservoir of the cell; have a low evaporation rate to insure the life of the cell; have a certain degree of selectivity for the pollutant; be chemically and physically inert to the electrolyte and the sample stream; and have a fast diffusion rate.

A fairly complete selection of membranes was assembled for evaluation.

a.) Permeability - The criterion of permeability eliminated many of these at the beginning of the tests. Formaldehyde would not permeate through:

- 1.) 1 mil polyvinyl chloride
- 2.) 1 mil polyvinyl acetate
- 3.) 1 mil cellophane
- 4.) 1 mil polyethylene
- 5.) 0.5 mil Kapton or H-Film
- 6.) 1.5 mil Mylar
- 7.) 1/4 mil Teflon

Membranes which were found to be permeable and their sensitivities are listed:

- 1.) 1 mil single backed dimethyl silicone, 1.5 μ A/ppm
- 2.) 1 mil silicone-polycarbonate (MEM 213) 2 μ A/ppm
- 3.) Permion 2291 -cation exchange membrane, drifted.
- 4.) 4 mil R.T.V. Silicone Rubber Cement, 1 μ A/ppm
- 5.) Zitex (Teflon hydrophobic fiber) 12-137A, pore size 1-2 μ , pore volume 12%, 2.7 μ A/ppm
- 6.) Zitex 12-137B, pore size 3-6 μ , pore volume 20%, 25 μ A/ppm
- 7.) Zitex - E606-223, pore size 1-2 μ , pore volume 55%, 2 μ A/ppm

These values were obtained using a 30 ml cell body which contained a 1.9" gold sensing electrode, 10% KOH electrolyte, a pressed Ag/Ag₂O counter-electrode, and an applied potential of +0.1 volt.

Zitex is a trade name used by Chemplast for their membranes made of fibrous hydrophobic teflon. It is a porous medium which seals the cell through a capillary effect. The mechanism by which a gas reaches the electrolyte is simple physical transport. There is no selectivity, all gases permeate at the same rate.

b.) Leakage - Of the permeable membranes, MEM 213 and RTV did not suffer any kind of leakage. The Zitex membranes often developed pinhole leaks especially at the O-ring seal of the cell. Permion did not hold back electrolytes at all. Single backed dimethyl silicone leaked consistently.

c.) Evaporation Rates

- 1.) 1 mil MEM 213 - 0.7g/dry
- 2.) 4 mil R.T.V. - Not determined.
- 3.) Zitex 12-137A - $\approx$ 7g/day (1.9" diameter)
- 4.) Zitex 12-137B - $\approx$ 12g/day (1.9" diameter)
- 5.) Zitex E606-223 - Not determined.

It was observed that membranes which transmitted CH_2O efficiently also allowed water to pass from the electrolyte to the sample stream. This property accounts for the relatively high evaporation rates. The tests were conducted with dry nitrogen at 80°F , at a flow rate of 1.0 SCFH. The cells contained 180 ml of electrolyte and had 1.9" diameter membranes. Use of partially humidified air would decrease these values by as much as 80%.

d.) Selectivity - Of the membranes listed in part c.) above, only MEM 213 and R.T.V. demonstrated any degree of selectivity. This selectivity was most apparent in the reduction of carbon monoxide and nitric oxide levels but it did not eliminate either of them completely. All of the pollutant gases permeated at rates capable of causing interference.

e.) Electrolyte Compatibility - Zitex membranes are composed of teflon fibers and thus are compatible with all aqueous electrolytes.

MEM 213 has long term stability in the pH range 4-9. However, its life time in 1N H_2SO_4 is at least 6 months based on previous studies. In 10% K_2CO_3 it was one month (pH 11.4); in 10% KOH it was only three days.

The fabricated R.T.V. silicone membrane was stable in all of the electrolytes.

f.) Relative Diffusion Rates - Based on tests in a variety of electrolytes the acceptable membranes demonstrated maximum response times of:

- 1.) MEM 213 - 90% in 1 to 3 minutes.
- 2.) R.T.V. - 90% in 30 minutes.
- 3.) Zitex - 12-137A - 90% in 2 minutes.
- 4.) Zitex - 12-137B - 90% in 3 minutes.
- 5.) Zitex E606-223 - 90% in 30 minutes.

These response times were obtained in cells containing 10% KOH, a $\text{Ag}/\text{Ag}_2\text{O}$ counterelectrode, a Au sensing electrode, and an applied potential

of +0.1V. The membranes were all 1.9" in diameter. The CH_2O concentration was 2.2 ppm CH_2O at a flow rate of 1.0 CFH. All tests were run at room temperature.

3.3.2 Development of Final Membrane

None of the membranes tested was suitable for formaldehyde detection. R.T.V. was too slow. MEM 213 was probably the best available but it was not compatible with any of the proposed electrolytes. This left only Zitex as a reasonable membrane surface.

The use of Zitex as a membrane has many drawbacks. The four most important are listed below.

1. Zitex is a porous medium. It is by this means that the sample gases are transported to the electrode. The partially vaporized electrolyte is transported with equal facility back to the sample gas stream. This heavy electrolyte loss drastically reduces the life-time of the cell.
2. It is very difficult for the manufacturer to maintain the uniformity of the teflon fiber structure of Zitex. Very often pin hole leaks develop which soon render the cell useless.
3. Zitex, being a teflon compound, is characterized by weeping at sealed surfaces. Thus the O-ring seal of the cell eventually becomes ineffective.
4. A high percentage of the sample is absorbed in the electrolyte when a Zitex membrane is used. This very often results in non-linearity at low concentrations where absorption decreases due to reduction in collision cross sections. The high surface area also is responsible for slow response times.

It was apparent that none of the three types of Zitex were acceptable as tested. An alternative method of approach was selected. Since the current was very high

for 12-137B it seemed obvious that a 90% reduction in surface area would still leave plenty of sensitivity. A membrane of 1 mil polyethylene, which is impermeable to formaldehyde, was cut to fit the cell. A 0.5" hole was cut in the center. A 0.7" diameter piece of 12-137B was bonded across the hole with epoxy cement. It was determined that this configuration had the following practical advantages over those previously tested.

1. The evaporation rate was reduced by an order of magnitude.
2. Weeping was not apparent since the O-ring seal was on the polyethylene membrane.
3. Linearity at smaller concentrations was achieved.
4. Response time was increased to 90% in 45 seconds.
5. Seepage was reduced significantly. It was determined that alot of the previous trouble was associated with the O-ring seal crushing the membrane.

Obviously this type of membrane was far superior to those previously tested. However, there were still some problems in the selection of the final support material. Polyethylene was found to make a weak bond with epoxy cement.

Other materials impermeable to formaldehyde were tested. 1.5 mil Mylar was strong but was subject to chemical corrosion. Polyvinyl acetate and polyvinylchloride stretched too much. The best support material was determined to be 2 mil teflon film. The surface of this membrane was treated with a sodium suspension. This treatment left a carbonized surface layer which provided a good adhesion area for epoxy cement. Other desirable properties were the strength and inflexibility of the 2 mil thickness which contributed greatly to the stability of the electrolyte layer between the membrane and the electrode.

3.4 Evaluation of Electrolytes

3.4.1 Screening Test and Results

The electrolyte is one of the most important components of the cell. Its selection is determined largely on the basis of the chemical and electrochemical properties of the electrolyte relative to formaldehyde. Chief among these are:

- 1.) Potential of Oxidation and Reduction Reactions - The electrolyte coupled with the sensing electrode determines the oxidation or reduction potential of formaldehyde.
- 2.) Reaction Rate - The electrolyte contributes generally to the improved kinetics of electrochemical reactions either through chemical reaction with the species, participation in the electrochemical reaction or as a catalytic agent.
- 3.) Reaction Scheme - The electrolyte determines, usually through chemical interaction, the extent to which an oxidation or reduction will proceed, that is to say, the number of electrons involved.
- 4.) Diffusion Rate - The rate of diffusion of formaldehyde through the electrolyte affects the rate of response. By holding the thickness of the electrolytic layer and the membrane material constant, comparative rates can be determined as a function of ion species and concentration. These determinations were not necessary since only the response rates were of interest.
- 5.) Absorption Rate - The magnitude of the response is a function of the percentage of pollutant which is absorbed at the membrane electrolyte interface.

Several electrolytes were evaluated as candidate medias for the selective oxidation of formaldehyde. Representative data is tabulated in Table I. Two types of sensing electrodes were used, 1.9" dia. gold and platinum. The platinum electrodes were

TABLE 1. ELECTROLYTE SCREENING STUDY

<u>Electrolyte</u>	<u>Sensing Electrode</u>	<u>Counter Electrode</u>	<u>Applied Voltage</u>	<u>Response Time 90%</u>	<u>Remarks</u>
1N H ₂ SO ₄	Au	PbO ₂	+0.9	6 min., 50 ppm	Insensitive, inefficient.
1N H ₂ SO ₄	Pt	PbO ₂	+0.6	3 min., 50 ppm	Inefficient
30% H ₂ SO ₄	Au, Pt	PbO ₂	None	None	
1N KCl	Au, Pt	Ag/AgCl	None	None	
10% KHCO ₃	Au	PbO ₂	None	30 min.	Very slow.
20% KHCO ₃	Au	PbO ₂	None	30 min.	Very slow.
20% KHCO ₃	Pt	PbO ₂	None	5 min.	
10% K ₂ CO ₃ +	Au, Pt	Ag/Ag ₂ O	None	5 min.	
10% KHCO ₃	Au	Ag/Ag ₂ O	-0.1	5 min.	Slowed with time.
10% K ₂ CO ₃	Pt	Ag/Ag ₂ O	-0.1	45 sec.	Pt catalyzed.
10% K ₂ CO ₃	Pt	Ag/Ag ₂ O	-0.1	30 sec.	Pt catalyzed.
2% K ₂ CO ₃	Pt	Ag/Ag ₂ O	-0.1	1 min.	Pt catalyzed.
20% K ₂ CO ₃	Au	Ag/Ag ₂ O	None	30 min.	
50% K ₂ CO ₃	Au, Pt	Ag/Ag ₂ O	None	1.3 min.	
2% KOH	Au, Pt	Ag/Ag ₂ O	+0.15	45 sec.	
10% KOH	Au	Hg/HgO	-0.1	15 sec.	
45% KOH					

platinum plated 333 line gold mesh. The response times reported were the fastest ones obtained. Each of the evaluations were conducted at room temperature. The membranes and counter electrodes were varied while recording these response times. The membranes were not reported because MEM 213 and reduced Zitex were the only ones used. The counter electrodes, although reported, were not necessarily the ones best suited to the electrolyte. The PbO_2 electrode was plated on a platinum mesh. All of the other counter electrodes were pressed electrodes, contained within a polypropylene skin, and supported by a suitable metallic mesh.

The concentration of formaldehyde used for the tests was 2 ppm in a stream of dry N_2 . Exceptions to this are noted. The formaldehyde source in all cases was a permeation tube. Electrolyte additives such as gelatin, mannitol, and potassium formate were ineffective in all of the tested solutions.

3.4.2 Discussion of Results

Sulfuric acid was found to be an entirely unacceptable oxidation medium. Preliminary studies with a commercial 37% formaldehyde solution used as the source of formaldehyde had not shown this. Subsequent work with this electrolyte revealed that the response attributed to formaldehyde oxidation was due entirely to the presence of the 13% methanol used as a stabilizing agent. Tests conducted with a solution containing only 13% methanol gave exactly the same response as the commercial formaldehyde.

Evaluation of 1.0 N H_2SO_4 sensors was then conducted with formaldehyde permeation tubes. This electrolyte was found to be insensitive to formaldehyde at concentrations below 10 ppm. At 50 ppm the oxidation at platinum and gold was very inefficient.

During the evaluation of these experimental transducers, it was observed that, after responding to formaldehyde, the cells never wholly recovered, i.e., an increase of the baseline current was always registered.

A cell's recovery, in some cases, would be smaller than 20% of the total response to formaldehyde. It was believed that the cause of the continuously increasing baseline current was unreacted formaldehyde. In other words, not all of formaldehyde permeating through the membranes was being electro-oxidized. In order to corroborate this assumption, CH_2O analyses using the chromotropic acid procedure were performed upon a number of electrolytes extracted from the experimental transducers. Although color development difficulties were encountered, it was possible to determine the existence of formaldehyde (5 to 80 ppm) in all of the tested electrolytes.

Elimination of sulfuric acid as an electrolytic medium created a need for additional development effort.

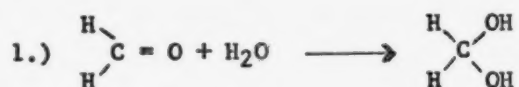
From the screening test results a very predictable problem was shaping up. The final sensor would be subjected to a 12-15% CO_2 environment. The only electrolytes which showed some promise for the rapid detection of formaldehyde were potassium carbonate solutions with platinum electrodes and potassium hydroxide solutions with gold on platinum electrodes. Both of these electrolytes are neutralized by CO_2 to bicarbonate. Potassium chloride and bicarbonate solutions which are not affected by CO_2 were not effective in the detection of formaldehyde. These findings were not surprising because they coincided very well with the sweep voltammetry studies.

The effect of electrolyte concentration on response time was determined from both K_2CO_3 and KOH solutions. The results were quite opposite. As the K_2CO_3 concentration increased the response time became slower. For KOH the response became dramatically faster. The answer to these results is found in the hydroxyl ion concentration which affects the rate of reaction at the sensing electrode. As the carbonate ion increases, the hydroxyl ion concentration does not become significantly greater and the high concentration slows the diffusion rate. An increase in the KOH concentration results in a direct increase in the hydroxyl

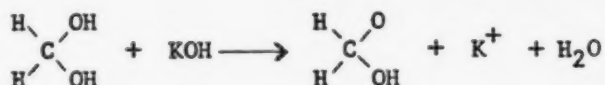
ion concentration. A corresponding increase in the rate of reaction was observed.

The role of the hydroxyl ion as an oxidation expediter also explains the results obtained in the screening tests and the sweep voltammetry experiments. As the pH value increases the electrolytes become increasingly effective in the detection of formaldehyde.

Formaldehyde goes into solution by combining with water to form the gem-diol.

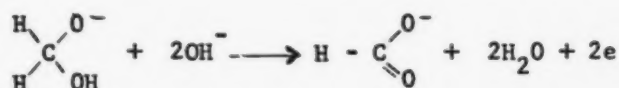


The gem-diol subsequently polymerizes and becomes unavailable for oxidation or it reacts to the potential at the sensing electrode. In a basic media reaction 1.) is immediately followed by or substituted by the reaction:



In this ionic form the diffusion rate is more rapid.

The basic media also holds the oxidation reaction scheme of formaldehyde to a one step process, the production of the formate.



This 2 electron oxidation was verified in a separate faradic experiment. In an acidic media the reaction proceeds all the way to the formation of CO₂, a 4 electron oxidation. This would seemingly enhance the sensitivity but the second oxidation step is so slow that it impedes the rate of response.

3.4.3 Electrolyte-Exhaust Stream Compatability Tests

Tests were conducted with a sample stream containing 12% CO₂ in dry N₂ to determine the neutralization rate of 10% KOH and 10% K₂CO₃ in magnetically stirred sensor cells.

During the first two weeks, it was observed that the neutralization rate of 10% KOH by 12% CO₂ decreased as a function of time from 0.23%/hr. to 0.05%/hr., calculations based on the original KOH configuration. It then stabilized at this rate and 58.4% was neutralized after six weeks. It was estimated that complete conversion would take place in about 4 to 5 months. It was postulated on the results of the concentration-response time tests that until complete conversion was achieved the oxidation potential or response time would not be dramatically affected. However, once complete conversion had been achieved a dramatic oxidation potential shift would occur. This shift might or might not be accompanied by an equivalent shift in the potential of the counter electrode. Most likely, neutralization would affect the selectivity of the cell and probably would effect the electrode kinetics.

In addition neutralization would not stop at this point. The resulting K₂CO₃ solution would be converted to the bicarbonate at a slightly slower rate. This rate is slow enough to guarantee a lifetime of 6 months before 50% of the electrolyte is converted to the bicarbonate. The formaldehyde response rate remains unaffected at this composition. With a Pt electrode the formaldehyde oxidation is retarded to 90% in five minutes in a solution completely converted to the bicarbonate. The exact point at which the bicarbonate conversion begins to affect the response time is not known.

This data applies only to neutralization of the entire cell. Oxidation and neutralization actually take place only in the thin electrolyte layer between the sensing electrode and the permeation membrane. Therefore, in the absence of agitation the complete neutralization of the cell would require a much longer period of time while complete neutralization of the thin electrolyte layer would depend on the CO₂ absorption rate, the hydroxyl ion concentration, and the diffusion rate of fresh hydroxyl ions to the electrode surface.

3.5 Evaluation of Counter Electrodes

3.5.1 Screening Tests and Results

A good counter electrode has at least three important characteristics:

- 1.) It has a stable potential, preferably close to or larger than that of the species to be oxidized.
- 2.) It is an efficient electrode made from an easily reduced species (in oxidation applications), having a large electrolyte-electrode interface surface.
- 3.) It is chemically and electrochemically compatible with the electrolyte.

From the results obtained in the electrolyte evaluations, it was clear that the final counter electrode would be used in only three solutions, KOH, K_2CO_3 and $KHCO_3$. All three of these solutions are basic and unfortunately very few electrodes have stable potentials in the basic pH range. Among the best couples are Hg/HgO and Ag/Ag₂O. The potentials of these two may vary as much as 10 mV. Since our need was not for precise reference electrodes this variance was tolerable. The combinations which were evaluated are presented in Table 2. All of the cells were assembled using reduced zytex membrane and a platinum sensing electrode.

The candidate counter electrodes were all pressed electrodes with the exception of PbO₂ which was plated on a platinum mesh. Each was fabricated from Analytically Pure Reagents, pressed at 8000 psi onto an appropriate metal support mesh, and enclosed within a polypropylene filter paper skin. The Hg/HgO electrode was tested both as a pressed electrode and in the form of a mercury pool.

From the results obtained it was concluded that either the bicarbonate media was a poor one for the oxidation of formaldehyde or that lack of a common ion effect was severely hampering the counter electrodes.

For the most part the lead electrodes exhibited steady potentials and response times but as a group they were classified as inefficient electrodes. The most efficient electrodes were mercury oxide and the silver compounds.

TABLE 2. COUNTER ELECTRODE SCREENING STUDY

COUNTER ELECTRODE	ELECTROLYTE	APPLIED POTENTIAL (VOLTS)	RESPONSE TIME	REMARKS
PbO	10% KOH	None	Slow	-----
PbCO ₃	10% KOH	None	2.6 Min.	Potential drift, signal decay
Pb ₃ O ₄	10% KOH	None	7.2 Min.	Very steady
PbO ₂	10% KOH	None	Slow	Plumbate formed
Hg/HgO	10% KOH	None	1.3 Min.	Looked good
Ag/AgCl	10% KOH + 0.1N KCl	None	2 Min.	Noisy, high background
Ag/Ag ₂ O	10% KOH	None	1.3 Min.	Noisy but good
PbO	10% K ₂ CO ₃	-0.2	3.8 Min.	Signal decay
PbO ₂	10% K ₂ CO ₃	None	5 Min.	Good potential
Pb ₃ O ₄	10% K ₂ CO ₃	None	6.1 Min.	Steady
PbCO ₃	10% K ₂ CO ₃	-0.2	Slow	-----
Hg/HgO	10% K ₂ CO ₃	-0.2	45 Sec.	Not consistent
Ag/Ag ₂ O	10% K ₂ CO ₃	None	45 Sec.	Some noise and contamination
Ag/AgCl	10% K ₂ CO ₃ + 0.1N KCl	-0.2	45 Sec.	Noisy
Ag/Ag ₂ O	10% KHCO ₃	None	Slow	Good potential
PbO ₂	10% KHCO ₃	None	Slow	High potential
Hg/HgO	10% KHCO ₃	None	Slow	-----

However, the mercury electrodes were prone to potential drift and the silver electrodes severely contaminated the cells.

3.5.2 Compatability and Fabrication Studies

The mercury-mercury oxide couple was compatible with KOH and K_2CO_3 electrolytes; however, it was subject to response time decay and potential drift. The mercury couple usually has a fairly stable potential so it was postulated that the method of construction was responsible for the drift. Experimentation was conducted to determine the best method of fabrication. A pressed electrode was found to be far superior to the mercury pool type. An electrode which maintained a relatively constant potential along with a rapid response time was assembled by the following method:

1. The support mesh was 33 line gold which had been treated with chromic acid cleaning solution followed by immersion in nitric acid. This cleaning procedure ensured a proper surface for subsequent amalgamation with mercury.
2. A platinum wire lead was then spotwelded to the gold.
3. The mesh was immersed in triple distilled mercury. The excess mercury was jarred loose from the mesh by impact.
4. The mesh was pressed at 5000 lbs/in. in a 1.4" dia. mold with a mixture of 4 gm red mercuric oxide and 200 mg of polypropylene powder (Hercoflat 135), at 100°C for 15 minutes.
5. The whole electrode was pressed inside a polypropylene filter paper skin to keep it intact.

This electrode had a potential of 0.12V in 10% KOH and 0.27V in 10% K_2CO_3 versus the hydrogen electrode. Response times of 45 seconds were obtained in cells made with both solutions for 1 ppm CH_2O . The cells had platinum sensing electrodes and reduced Zytex membranes. No applied potential was used in KOH. A potential of -0.18V was used with K_2CO_3 .

Improvement of the silver compound electrodes was a more difficult task. It was discovered that Ag_2O and AgCl were not compatible with 10% K_2CO_3 . These compounds were slowly converted to silver carbonate. In addition, the silver electrodes were quite soluble in both KOH and K_2CO_3 . The silver ion would then migrate to the sensing electrode area and react with formaldehyde to deposit free silver on the membrane and sensing electrode. Contamination of the sensing electrode and membrane was stopped by inserting a layer of permion 2291, a cat on exchange membrane, between the two electrodes. This arrangement temporarily solved the problem until the permion was saturated. It was quite apparent that the silver was much more soluble under these conditions than the literature had reported.

During the course of these experiments it was noticed that the Ag_2CO_3 electrodes were discoloring as if they had been exposed to a light source. It was evident that the silver ions were being exposed to light through the opaque polypropylene cell body. This caused the formation of free silver, which in turn caused a concentration gradient of silver ion, which ultimately resulted in increased solvation of the counter electrode. To circumvent this problem the cell bodys were painted black. To further lower the solubility a counter electrode was made from AgCl pressed onto a silver mesh and KCl was added to the KOH and K_2CO_3 electrolytes to make the silver ion concentration smaller through the common ion effect. This last step did help clean the cell immeasurably. However, the presence of chloride in the electrolyte made the cell very noisy and increased the background current to $3 \mu\text{A}$. This was due to oxidation of the sensing electrode which occurs at much lower potentials in a chloride media. This sensitivity eliminated the AgCl counter electrode since it was not stable in the absence of chloride ion.

Silver carbonate was eventually eliminated because its solubility product was too high even in a 10% K_2CO_3 solution.

The Ag/Ag₂O electrode was clearly the only silver electrode which was useful and it could only be used in a KOH medium.

The best Ag/Ag₂O couple was obtained by pressing 4 gm of Ag₂O onto a silver mesh which had been immersed in 50% nitric to partially oxidize the surface. It was pressed at 18,000 lb/in² for 15 minutes.

The resulting electrode was noise free. The black cell reduced the solubility of the silver as anticipated. Even with the decreased solubility Permion 2291 still had to be inserted between the two electrodes. It was eventually discovered that this membrane inhibited adequate diffusion of the electrolyte to the membrane. This was characterized by 0.02 μ A spikes at 20 to 30 minute intervals due to localized depletion of electrolyte at the sensing electrode surface. These spikes were equal to a 1% noise level at the most sensitive range.

A separate experiment was conducted to determine the effect of applied potential on the Hg/HgO and Ag/Ag₂O electrodes. It was found that the potentials remained unaffected by exterior applied potentials. The only affects on the rate of response were due to the added resistance in the exterior circuit from the pot used to adjust the voltage.

3.6 Evaluation of Sensor Electrodes

3.6.1 Platinum Electrodes

Platinum electrodes were proven to be faster and more efficient than gold electrodes in every electrolyte except 10% KOH. Because of this superiority an experimental program was completed to bring the rate of response to a maximum with respect to the platinum electrode. The medium chosen was K₂CO₃ since it was the fastest electrolyte next to KOH and it offered more resistance to CO₂ poisoning than KOH. All of the platinum sensing electrodes tested were platinum plated gold with one exception - an 80 line platinum mesh. The test was conducted in two phases:

the effect of plating on response time and the effect of post-plating electrode conditioning on response time.

Plating conditions were varied quite widely during the test. Two different types of baths were used. The first was chloroplatinic acid at various concentrations in a solution buffered with diammonium phosphate and disodium phosphate. The second was a solution of the dinitroamine in sulfamic acid and water. This is manufactured by Sel-Rex Corp. under the trademark Platinex III. The test conditions and findings are presented in Table 3.

The best results were obtained with a 15 g/l chloroplatinic acid bath at a current density of 30A/ft³. The finish obtained under these conditions was found to be dark spongy platinum black. Electrodes plated under other conditions were, for the most part, irreproducible and exhibited erratic behavior during testing.

A series of experiments was initiated to chemically treat the platinum electrodes to improve their behavior. The specific areas where improvements were needed were: 1. The background current, which was very high. 2. The noise level, which was also too high, and 3. The response rate. The tests are outlined in Table 4. All of the experiments were conducted on platinum electrodes plated under the conditions in Table 3, item 1.

The best results were obtained with method 5 where the electrode was oxidized and cleaned in hot chromic acid and reduced in 20% FeSO₄. Cells made with this electrode, a Ag/Ag₂O counter electrode, reduced zirconium membrane and 10% K₂CO₃ had response times of 90% in 40 seconds and were virtually noise free.

A cell was constructed using a sensing electrode composed of 80 line platinum mesh. The purpose of this experiment was to determine the reaction time of a shiny, unblemished platinum surface. The response time for this electrode was extremely slow, 90% in one hour. This result lends credence to the possibility

TABLE 3. EFFECT OF PLATINUM PLATING ON RESPONSE TIME

<u>SUBSTRATE</u>	<u>PLATING SOLUTION</u>	<u>CURRENT DENSITY</u>	<u>90% RESPONSE TIME</u>	<u>REMARKS</u>
1. 333 11ne Au	15g/1 H ₂ PtCl ₆	30 A/ft ²	37-50 sec.	Initial high background current.
2. 333 11ne Au	10g/1 H ₂ PtCl	30 A/ft ²	1 min.	Very consistent
3. 333 11ne Au	4.0g/1 H ₂ PtCl ₆	10 A/ft ²	1-5 min.	Not reproducible
4. 333 11ne Au	Platinex III	10 A/ft ²	2 min.	----
5. 100 11ne Au	10g/1 H ₂ PtCl ₆	10 A/ft ²	1-2 min.	Not reproducible
6. 100 11ne Au	Platinex III	10 A/ft ²	2-5 min.	Not reproducible
7. 333 11ne Au	6g/1 H ₂ PtCl ₆	1 A/ft ²	3-5-min.	Slow and erratic
8. 333 11ne Au	6g/1 H ₂ PtCl ₆	3 A/ft ²	3-5 min.	Slow and erratic
9. 33 11ne Au	10g/1 H ₂ PtCl ₆	3 A/ft ²	30 min.	Much too slow

TABLE 4. CHEMICAL TREATMENT OF PLATINUM ELECTRODES

<u>Oxidizing, Cleaning Solution</u>	<u>Passivation Method</u>	<u>Reduction Method</u>	<u>Remarks</u>
1. Boiling 50% HNO ₃	Hot 40% KOH	None	Slower response, lower noise level and background.
2. Boiling 50% HNO ₃	Hot 40% KOH	Cathodic in 40% KOH	High background, 90% in 2 minutes.
3. Boiling 50% HNO ₃	None	Cathodic in 1N H ₂ SO ₄	High background, 90% in 40 seconds.
4. Hot Chromic Acid	None	Boiling HCl	Low noise and background, slower response.
5. Hot Chromic Acid	None	20% FeSO ₄	Very low background, low noise level, 90% in 40 seconds.

that the detection surface be of a fine grained nature either through deposition or chemical etching.

3.6.2 Gold Electrodes

Previous experiments with gold electrodes demonstrated their relative lack of efficiency when compared to platinum electrodes in 10% K_2CO_3 . The best response time obtainable was 90% in five minutes. In a 10% KOH medium their performance is comparable.

The chief value of a gold electrode lies in its low background current and noise level. Since these properties were of chief concern, electrodes of 333 line and 100 line gold were physically, chemically, and electrochemically treated with the hope of increasing the rate of response to formaldehyde. This goal was not achieved in the 10% K_2CO_3 electrolyte.

The explanation of this was demonstrated previously in figures 7 and 8. The formaldehyde oxidation curve for gold is broad with a gentle slope indicating a slow reaction. The curve for platinum is quite the opposite. The peak at 0.001 V is fairly sharp. In addition, a catalytic oxidation peak occurs around 0.4 V. Above this voltage the formaldehyde response is very rapid for platinum. Below 0.4 V the response time decreases to 90% in two to three minutes.

The methods for conditioning the gold for this test were essentially the same as for platinum with two exceptions: the gold was mechanically cleaned by scraping and thermally cleaned by pyrolyzation at 900°C. The calcinated gold electrode was found to be unresponsive to formaldehyde. The fastest rate of response was the limiting value of 90% in five minutes. It was clear that gold was of little use in 10% K_2CO_3 solutions. Its chief value was in applications in 10% KOH.

3.6.3 Palladium and Rhodium Electrodes

Palladium and Rhodium electrodes were prepared from solutions of Palladex and Rhodex manufactured by Sel-Rex Corp. These electrodes were similar to

gold in response times but were characterized by high background currents. Sweep voltammetry curves using these electrodes indicated that oxidation of the base metals was occurring.

3.6.4 Sensing Electrode-Exhaust Stream Compatibility Studies

With the zitex membrane the sensing electrode is exposed to all of the contaminants in the exhaust stream. Thus the only selectivity exhibited by the cell would be due to:

1. The absorption rate of the electrolyte.
2. The potential of the sensing electrode.
3. The sensitivity of the sensing electrode.

A preliminary interference test was conducted with the major components of the exhaust stream: 2000 ppm NO, 200 ppm NO₂, 100 ppm SO₂, 2% CO, 3% O₂, and 12% CO₂. The tests were conducted with a gold electrode in 10% and 45% KOH and with platinum and gold electrodes in 10% K₂CO₃.

a.) CO₂ Interference - Solutions of 45% and 10% KOH were not compatible at all with 12% CO₂. With 45% KOH the carbonate was forming inside the membrane. This broke the surface tension of the solution which destroyed the hydrophobic nature of the zytex membrane. As a result crystals of carbonate grew right out of the top of the membranes. With 10% KOH the solution was converted to the bicarbonate medium as fast as the hydroxyl ions could diffuse back into the electrolyte layer. The same results were obtained with 10% K₂CO₃. The sensing electrode in each case lost sensitivity. This was not due to the reaction of CO₂ with the electrode but to the reaction of CO₂ with the electrolyte layer.

Since there was no alternative in the choice of electrolytes or membranes, experiments were conducted to see if this problem could be solved through sampling techniques. It was determined that a ten-fold dilution of the exhaust stream would lower the CO₂ level to the point

where neutralization of the electrolyte was not faster than diffusion of hydroxyl ions to the electrode oxidation site. This method was deemed adequate in view of the fact that a ten-fold dilution of the sample would also result in lowering the dew point of the sample (in this case, automobile exhaust) below room temperature. This would prevent water condensation and subsequent formaldehyde loss in the condensate.

b.) CO Interference - The platinum electrode in the K_2CO_3 cell was found to be extremely sensitive to carbon monoxide whereas the gold was not. The interference from 2% CO was equivalent to 10 ppm CH_2O and could not be eliminated through potentiostatic control. This turn of events eliminated K_2CO_3 as a sensing media due to the 5 minute time limit imposed by oxidation kinetics at the gold electrode. The sensitivity of the platinum electrode to carbon monoxide was found to be due to an intermediate formed with platinum oxide at the electrode site.

c.) NO , NO_2 , O_2 , and SO_2 Interferences - In 10% KOH, interference from all of these components was eliminated at a controlled potential of 0.17V (NHE). In 45% KOH, the potential was 0.1V with respect to the hydrogen reference electrode. The interference from SO_2 could not be eliminated in the 10% K_2CO_3 medium. Interference from NO , NO_2 and O_2 were eliminated at +0.45 V (NHE).

3.7 Experimental Transducers

The difficulties encountered during the early stages of development prompted some experimentation with transducers of various configurations. While none of these configurations were successful they are recorded here for reference.

a.) Indirect Electrochemical Detection of Formaldehyde - The purpose of this cell was to enhance the response time to formaldehyde by means of the chemical reaction of formaldehyde with silver ion to form free silver. The silver formed would be reoxidized to silver ion at the

sensing electrode in proportion to the formaldehyde concentration. This test was conducted with two separate approaches: the first with Tollen's Reagent as the electrolyte, and the second with Ag_2O as the sensing electrode. The indirect concept was abandoned because the potential at the sensing electrode necessary to reoxidize the silver was also sufficient to oxidize all of the other pollutant gases. This property did not permit the cell to be selective.

b.) The Galvanic Cell - The Galvanic concept of two separate compartments for the sensor and counter electrodes was investigated for two main reasons: 1) it would permit the construction of wet counter electrodes which would not be hampered by the effects of high temperature compression and organic binders, and 2) the electrolytic bridge between the two compartments would prevent contamination in either direction. The experiment was concluded when it was found that the impedance caused by the electrolytic bridge made the cell very sluggish.

3.8 Selection of the Final Cell Configuration

By combining the results gathered in sections 3.3 - 3.6 reasonable configurations can be assigned to the final formaldehyde transducers. At least two different configurations are necessary, one for an analysis in a CO_2 environment, namely automobile exhaust, and another in the absence of a CO_2 environment, namely ambient air.

The following cell configurations were selected for prototype characterization:

a.) CO_2 Environment -

Membrane - Reduced Zitex 12-137B 0.5" dia.

Sensing Electrode - 333 line Au treated with 50% HNO_3 and 45% KOH

Electrolyte - 10% KOH

Counter Electrode - Hg/HgO or $\text{Ag}/\text{Ag}_2\text{O}$

Applied Potential - $-0.04V$ for Hg/HgO or $+0.15$ for Ag/Ag₂O.

Precautions - Black cell and Permion 2291.

b.) Ambient Environment

Membrane - Reduced Zitex 12-137B 0.5" dia.

Sensing Electrode - 333 line Aug.

Electrolyte - 30-45% KOH

Counter Electrode - Hg/HgO

Applied Potential - $0.1 V$

For the CO₂ environment the option of using a Ag/Ag₂O electrode was included. Ag/Ag₂O although slightly noisy is a much better working electrode under a wide variety of electrolytic conditions. It may also be necessary to change the applied potential as the electrolyte layer becomes neutralized.

4.0 PROTOTYPE CHARACTERIZATION

4.1 Interference Studies

4.1.1 Signal Interference

a.) Cell for Auto Exhaust - The initial transducer contained a 10% KOH electrolyte and a Hg/HgO counter electrode. The cell was preconditioned with 1% CO₂ in between interference tests with various gases. It was determined that the magnitude of interference due to each pollutant for a 10% KOH cell did not change appreciably in the presence or absence of CO₂. However, to achieve selective oxidation it was necessary to increase the applied potential of the cell during CO₂ exposure from $-0.04 V$ to $-0.1V$ for a Hg/HgO counter electrode. During the course of the study it was noticed that the Hg/HgO electrode often became sluggish when faced with the task of oxidizing formaldehyde in a partially carbonated media.

Tests with a $\text{Ag}/\text{Ag}_2\text{O}$ electrode and an applied potential of +0.13 V indicated that it was not affected by partially carbonated conditions. The interference data is presented in Table 5. Results were the same for both counter electrodes.

The quantitative results of the study proved to be very satisfactory. Interference from the major contaminants proved to be almost nil. The largest interference was obtained from NO_2 . However, the maximum value for this proved to be only 2% on the most sensitive scale.

The partially oxidized hydrocarbons had high interference values. This was to be expected. However, it was determined that alcohols and ketones have a higher oxidation potential than aldehydes at a gold electrode. Thus interference from these compounds is minimal. The detection cell was equally sensitive to all of the aldehydes included in the test. Each was found to have a response comparable to formaldehyde. Response rates were also the same.

b.) Ambient Cell - Interference studies with the ambient cell containing a Hg/HgO counter electrode yielded even better results. A 30% KOH solution was used for the electrolyte, since response times of 15 sec. for 90% were obtained using this electrolyte.. The signal-interference test results for the ambient cell are listed in Table 6.

Interferences from SO_2 and NO_2 were greatly reduced, as were signal levels from other pollutant species. The number of partially oxidized hydrocarbons was reduced for this study. Only one compound representing each of the species was evaluated. The Hg/HgO electrode appeared to be a much faster and more stable counter electrode in the more concentrated basic electrolytes than it had been in the partially carbonated dilute bases.

TABLE 5
SIGNAL INTERFERENCE DETERMINATIONS
EXHAUST CELL

<u>Gas</u>	<u>Concentration</u>	<u>Equiv. ppm of CH₂O</u>
CO	2%	0.0
O ₂	5%	0.0
SO ₂	100 ppm	2.97×10^{-3}
NO ₂	200 ppm	2.0×10^{-2}
NO	2000 ppm	0.0
CO ₂	1%	0.0
CH ₄	100 ppm	0.0
C ₂ H ₆	100 ppm	0.0
C ₂ H ₂	100 ppm	1×10^{-5}
Hexane	500 ppm	8.8×10^{-5}
Acetaldehyde	10 ppm	10.0
Propional	10 ppm	10.0
Acrolein	10 ppm	10.0
Acetone	10 ppm	0.0
2-Butanone	10 ppm	6.1×10^{-2}
Benzaldehyde	10 ppm	10.0
Methanol	10 ppm	6.4×10^{-3}

TABLE 6
SIGNAL INTERFERENCES,
AMBIENT CELL

<u>Gas</u>	<u>Concentration</u>	<u>Equiv. ppm of Formaldehyde</u>
CO	2%	0.0
O ₂	5%	0.0
SO ₂	100 ppm	1×10^{-4}
NO ₂	200 ppm	2×10^{-4}
NO	2000 ppm	0.0
CH ₄	100 ppm	0.0
C ₂ H ₆	100 ppm	0.0
C ₂ H ₂	100 ppm	0.0
Hexane	500 ppm	1×10^{-4}
Benzeldehyde	10 ppm	10.0
Methanol	10 ppm	8×10^{-4}
Acetone	10 ppm	0.0

4.1.2 Physical Interference

Physical interference from pollutants indigenous to an exhaust stream was observed in only two cases. The first was in the presence of water, the second was due to CO_2 .

a.) Water - Water interferes with the detection of formaldehyde when the relative humidity is higher than 30-50%. If the gas stream temperature is below its dew point condensed moisture in the sample chamber of the cell completely prevents the detection of formaldehyde at any concentration. Humidity levels at 90 to 95% reduced the signal level at 1 ppm by 25% and slowed the response time to 90% in 10 minutes. A relative humidity of 70% caused a 7% signal loss at the 1 ppm level. Since the exhaust stream dew point is about 120°F problems with moisture are anticipated unless the sample is diluted. Removal of water from the sample stream would also remove the formaldehyde.

b.) CO_2 - Interference from CO_2 was determined at the 1% level. It had been previously determined that a level of 12-15% CO_2 could not be tolerated in direct contact with the cell. At 1% concentrations, the behavior of the 10% cell with a Hg/HgO counter electrode was steady for a continuous period of four hours. After this period the formaldehyde signal level was observed to drift. A 24 hour exposure caused the signal to decrease to 20% of its original value. The response rate also decreased to 90% in 10 minutes. With a Ag/Ag₂O electrode the signal decay was much less intense for long periods, about 10%, and the 90% response time remained fairly constant at 1 minute. Discontinuous use of either cell in the presence of 1% CO_2 did not cause any of these problems. It was also observed that cells badly damaged through continuous exposure would recuperate after a period of flushing with a zero gas of air or nitrogen.

Ambient cells were exposed to 300 ppm CO₂ and 1000 ppm CO₂ for long periods of time without any apparent damage.

4.2 Stability Tests

Results of tests with 1% CO₂ carrier gas streams were reported in section 4.1.2. Both cells were also tested with uncontaminated N₂ carrier gases. The exhaust stream cell had a Ag/Ag₂O electrode, the ambient, a Hg/HgO electrode. The cells were evaluated by testing them in a temperature chamber which was set at 80°F. Variation in temperature was occasionally +5°F. The cells were continuously exposed to a N₂ gas stream containing 2.2 ppm formaldehyde at 1.0 SCFH. The signal was continuously monitored with a 10 mV recorder. Twice a day the cells were flushed with pure nitrogen and the zero signal was recorded.

4.2.1 Span Drift

Span drift for both cells was almost negligible. Initial variations were ±2%/day. However, after 4 days the cells stabilized to ±1%/day.

4.2.2 Zero Drift

Initial zero drift was due to stabilization of the cell after construction. Upon reaching equilibrium both the 10% KOH and 30% KOH cells showed very little tendency towards zero drift. Values of ±1%/day were recorded.

4.2.3 Noise Level

The noise level for the ambient cell was negligible. The exhaust cell contained a Ag/Ag₂O counter electrode which was prone to random electro chemical discharges. After equilibration these indiscriminate noise levels were reduced to a 2% signal level.

4.3 Linearity

Tests were conducted to demonstrate the linearity of the detection current generated by the cell at varying concentrations of formaldehyde. The transducer was the Hg/HgO-KOH standard ambient cell. The membrane used was the reduced area Zitex 12-137B on a teflon substrate.

The test was conducted at 80°F. The results are presented in Figure 16. Values were taken at 0.5, 1.0, 2.0, 5.0, and 10.0 ppm formaldehyde. When normalized to a signal for 1 ppm formaldehyde the variation was found to be $\pm 0.5\%$, increasing from a value of 2.16 $\mu\text{A/ppm}$ at 0.5 ppm to 2.18 $\mu\text{A/ppm}$ at 10.0 ppm.

4.4 Temperature Effects

4.4.1 Signal Interference

Electrochemical transducers are very sensitive to temperature variations. An experiment was conducted in an environmental chamber on two samples of each formaldehyde monitor. Current readings were taken in the range 65°F to 110°F. The sample stream was 2.2 ppm formaldehyde in nitrogen. Typical current-temperature curves are shown in Figure 17.

4.4.2 Physical Interference

At temperatures lower than 60°F formaldehyde condensation and polymerization take place. This phenomenon is due both to the properties of formaldehyde and to the lowering of the dew point of the gas stream. Because of this characteristic the cell will be temperature controlled at 80°F. Above 80°F temperature compensation will be utilized. Use of temperature compensation corrected the curve detailed in Figure 17 to a straight line normalized to the current value at 77.5°F. This was accomplished through the use of a thermistor in series with a resistor of equal value in the feedback loop of the first stage amplifier in the instrumentation package.

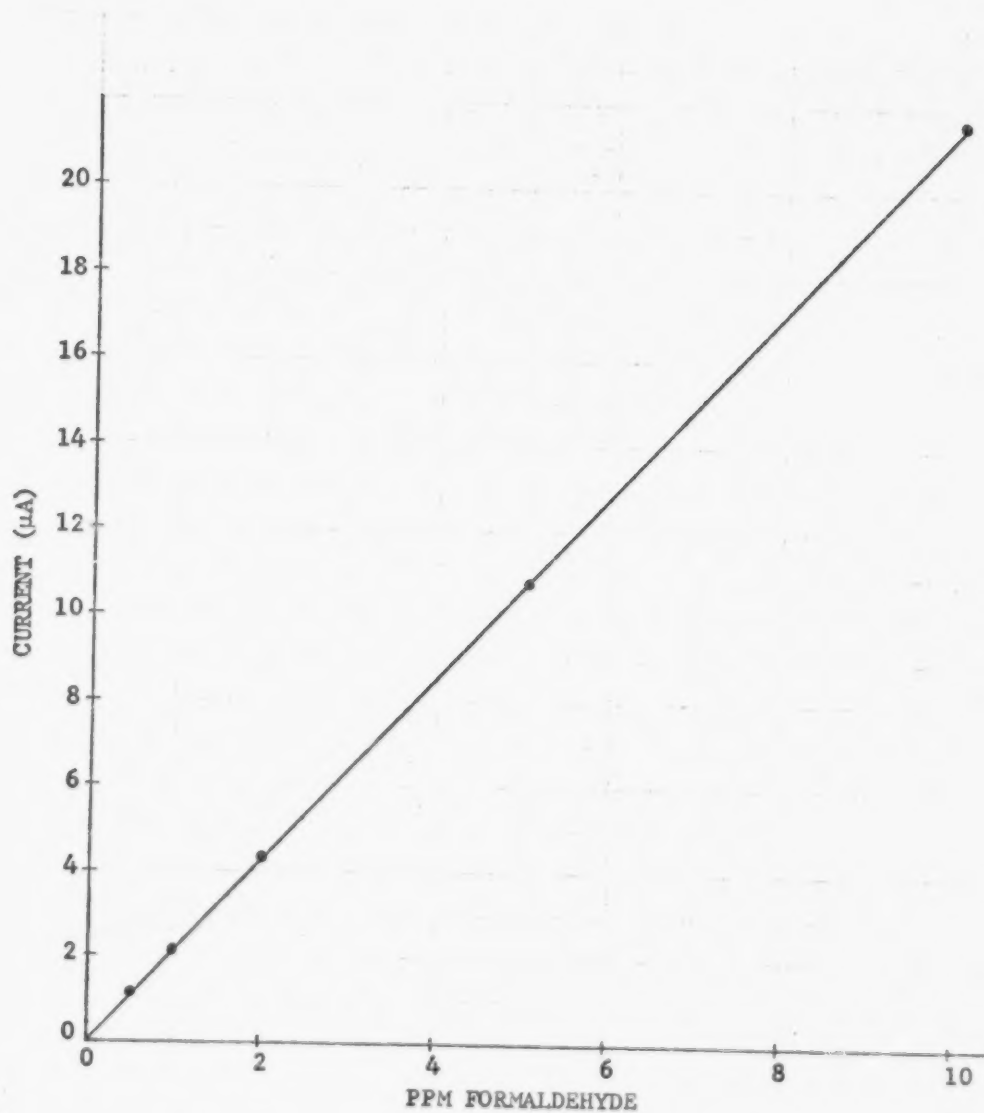
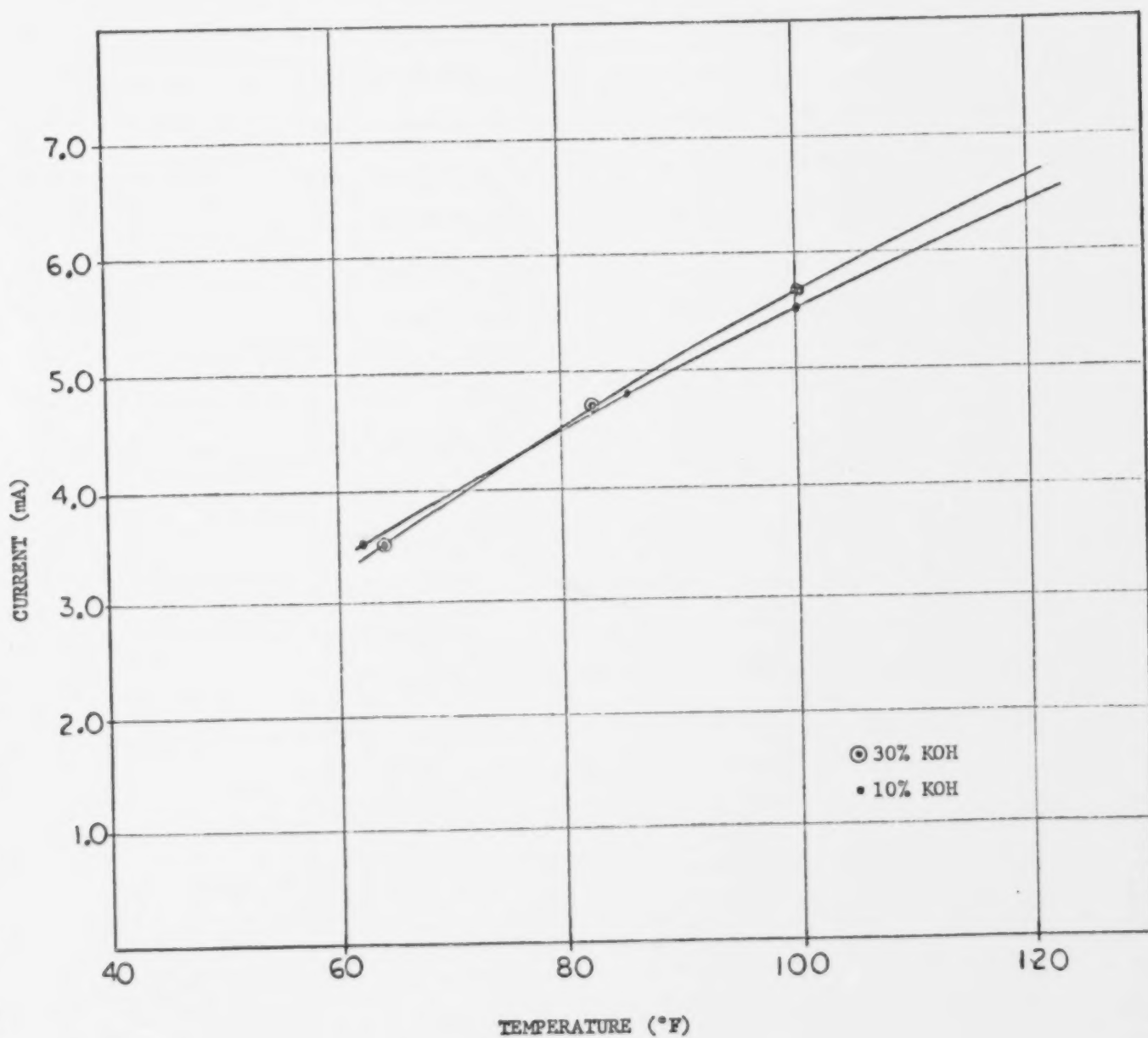


FIGURE 16 FORMALDEHYDE CONCENTRATION
VERSUS DETECTION CURRENT

FIGURE 17
CURRENT OUTPUT VERSUS TEMPERATURE FORMALDEHYDE CELL



4.5 Life Time

The life time of a cell is dependent on each of the individual components. The electrolyte supply in the cell was determined to be adequate for eight months of continuous use. This figure is based on a weight loss of 0.5g/day with dry N₂. With a semi-humid gas stream the cell should last longer.

Samples of the counter electrodes have been operational for six months without any signs of deterioration.

The life time of the sensor electrode depends on the rate at which it is poisoned. The Hg/HgO counter electrode and the gas stream pollutants have not affected the electrode. The Ag/Ag₂O might possibly present some problems but as yet these have not materialized.

The membrane is composed almost entirely of teflon and is not expected to be damaged.

4.6 Evaluation of Sampling Techniques

4.6.1 Redesign of Cell Sample Area

The sample chamber of the standard cell was not adequate for the determination of formaldehyde. It had too many surfaces where formaldehyde could condense out, too long a residence time, and it allowed most of the formaldehyde to pass through without coming into contact with the membrane surface. Response times using this chamber were 90% in 10 minutes at 0.1 μ A/ppm. See drawing 672020 in the appendix.

The chamber was redesigned to eliminate these deficiencies. The volume of the chamber was decreased in size by 80% to lower the residence time. The electrode support screen was removed to decrease the available condensation surface area and to allow the entire formaldehyde sample to flow over the membrane surface. Support for the sensing electrode was achieved through the use of a porous 1.5" teflon pad for the exhaust cell and a 1.9" diameter nylon mesh for the ambient cell.

The diameter of the reduced zytex membrane was enlarged to 0.75" for the auto exhaust cell. This increased the sensitivity of the cell to 5 μ A/ppm so that the sample could be diluted. The diameter of the ambient cell membrane was decreased to 0.4". This increased the response time, decreased the evaporation rate, and reduced the sensitivity for ambient studies to 1.4 μ A/ppm.

4.6.2 Ambient Sampling Conditions

For the ambient cell there are no special problems. Sampling should be conducted under the following conditions:

- 1.) The sample should be in the 80-120°F temperature range, preferably around 80°F.
- 2.) The sample stream should be free of particles larger than 100 μ .
- 3.) The flow rate should be 1-2 CFH.
- 4.) The relative humidity should be around 50% or lower. Above 50% some formaldehyde condensation takes place.
- 5.) The sample should be pushed through rather than pulled. Pulling the sample through may increase the response time.

4.6.3 Auto Exhaust Sampling Conditions

The exhaust stream cell is quite adequate when used in the proper manner.

- 1.) The exhaust sample should be diluted to lower the CO₂ level to 1%. This can be accomplished by physically mixing a 1 SCFH sample of the exhaust stream with a 9 SCFH air flow and subsequently metering a 1 SCFH sample of the mixture through the cell.

The preferred method would be to utilize a venturi type pump which would suck in a 1 CFH sample of the exhaust at a flow rate of 9 CFH. A 1 CFH sample of this mixture could then be pushed through the cell.

A second alternative would involve sampling the gas stream with a permeation membrane such as MEM 213. The diffused gas would then be passed through the cell with an air stream at 1-2 CFH.

The final condition of the sample should be the same as for the ambient cell.

The testing should be conducted on a discontinuous basis. The cell will usually function without problems if it is exposed to the diluted exhaust stream for 0-30 minute periods followed by a 10 minute purge with air.

APPENDIX A

INSTRUMENT OPERATION AND DESIGN

APPENDIX A
INSTRUMENT OPERATION AND DESIGN

The Dynasciences Formaldehyde Monitor is a compact, portable instrument designed for rapid discontinuous measurements of the concentration of formaldehyde in a diluted automobile exhaust stream (AL-620). It may also be used for continuous measurements under ambient conditions (AL-610). Front, top, and side schematic views of the monitor are shown in drawing No. 620551. Other pollutants that can be measured by substituting the appropriate selective transducer into the instrument package are: oxides of nitrogen, nitrogen dioxide, sulfur dioxide, and undiluted ambient formaldehyde. This interchangeability is an outstanding feature which makes the monitor a highly versatile tool.

The model numbers, standard ranges and the recommended applications of the different sensors are as follows:

	<u>MODEL</u>	<u>GAS MEASURED</u>	<u>RANGES:</u>	<u>APPLICATION</u>
1.	NX-130	Total oxides of nitrogen*	0-500, 0-1500 and 0-5000 ppm	Industrial stacks, automobile exhaust, process control, development studies.
2.	SS-330	Sulfur Dioxide	0-500, 0-1500 and 0-5000 ppm	Industrial stacks, process control, development studies.
3.	NR-230	Nitrogen Dioxide	0-200, 0-600 and 0-2000 ppm	Process Control
4.	NX-110	Total oxides of nitrogen*	0-5, 0-15 and 0-50 ppm	Plume and ambient measurements, exposure studies.
5.	SS-310	Sulfur Dioxide	0-1, 0-3, and 0-10 ppm	Plume and ambient measurements, exposure studies.
6.	NR-210	Nitrogen Dioxide	0-5, 0-15, and 0-50 ppm	Plume and ambient measurements, exposure studies.
7.	AL-610	Formaldehyde	0-1, 0-3, and 0-10 ppm	Ambient studies.
8.	AL-620	Formaldehyde	0-0.1, 0-0.3, and 0-1.0 ppm	Diluted automobile exhaust, ambient studies.

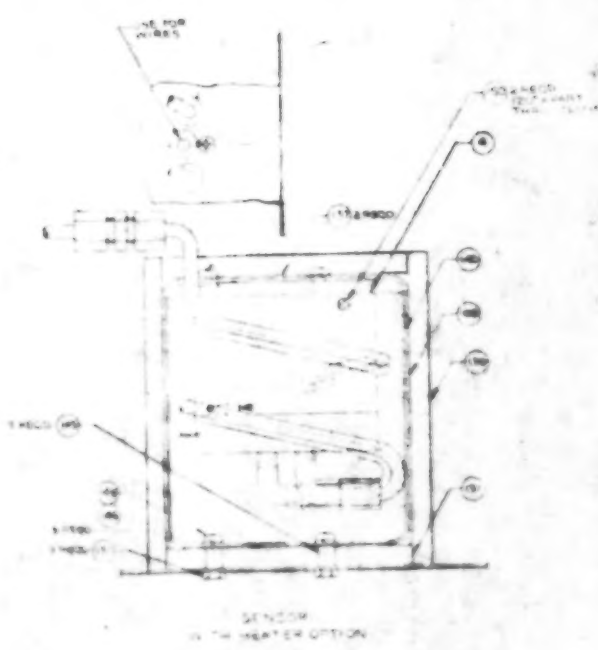
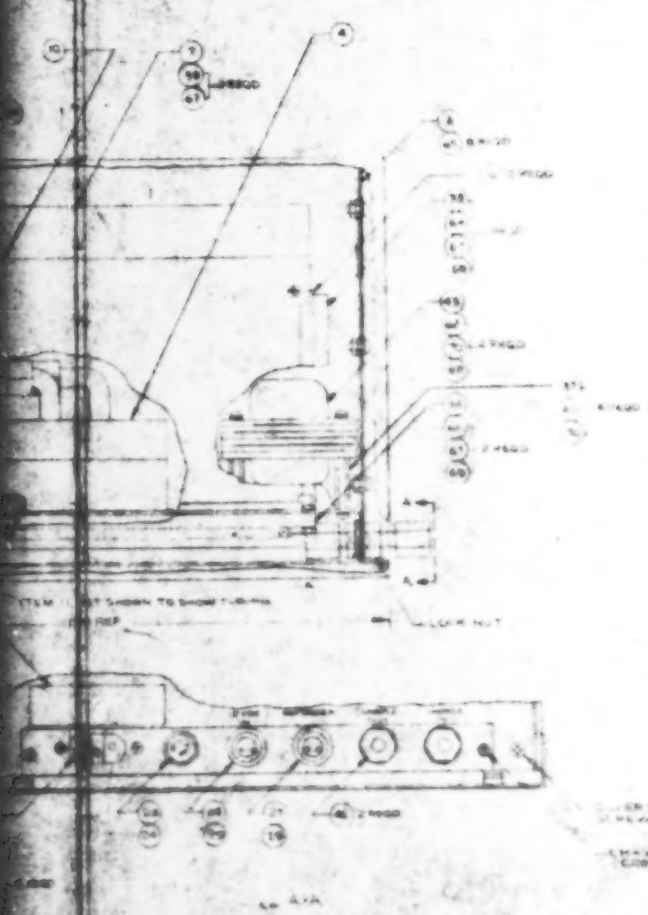
*Requires scrubber if SO₂ present.

Table 1A shows the specifications for Monitors AL-610 and AL-620.

TABLE 1A

MONITORS AL-610 AND AL-620 SPECIFICATIONS

Sensitivity Ranges:	0-1, 0-3, 0-10 ppm (AL-610) 0-0.1, 0-0.3, 0-1.0 (AL-620)
Detection Limit:	2% of full scale
Response:	Linear response over the entire range of the pollutant. Overall accuracy: $\pm 2\%$ full scale with the use of integral meter, $\pm 1\%$ full scale with the use of external potentiometric recorder.
Response and Recovery Times:	90% of full scale in less than 30 seconds (AL-610). 90% of full scale in less than 60 seconds (AL-620).
Stability:	Better than $\pm 1\%$ of full scale per day.
Specificity:	No response to N_2 , O_2 , CO, CO_2 , SO_2 , NO, water vapor or hydrocarbons.
Temperature Control:	About $80^\circ F \pm 1\%$.
Temperature Compensation:	$80^\circ F - 120^\circ F$.
Output:	Meter readout and 0-10 mV output for recorder.
Sensor Life:	One year at $80^\circ F$, moist gases
Power Supply:	105 to 125V 60 Hz 5 VA required for powering solid state amplifier (12 V.D.C. optional).
Monitor Weight:	Less than 15 lbs.
Flowrate:	Keep the flow rate within the green indicator on the flow meter. Recommended flow rate: 1 SCFH.



1. $2x^2 + 3x - 5$
 2. $4x^2 + 5x - 6$
 3. $6x^2 + 7x - 8$
 4. $8x^2 + 9x - 10$

1. NAME OF THE PERSON OR FIRM 2. ADDRESS 3. CITY 4. STATE 5. ZIP CODE 6. PHONE NUMBER 7. FAX NUMBER 8. TELETYPE NUMBER 9. COUNTRY 10. COMMENTS		11. NAME OF THE PERSON OR FIRM 12. ADDRESS 13. CITY 14. STATE 15. ZIP CODE 16. PHONE NUMBER 17. FAX NUMBER 18. TELETYPE NUMBER 19. COUNTRY 20. COMMENTS	
21. NAME OF THE PERSON OR FIRM 22. ADDRESS 23. CITY 24. STATE 25. ZIP CODE 26. PHONE NUMBER 27. FAX NUMBER 28. TELETYPE NUMBER 29. COUNTRY 30. COMMENTS		31. NAME OF THE PERSON OR FIRM 32. ADDRESS 33. CITY 34. STATE 35. ZIP CODE 36. PHONE NUMBER 37. FAX NUMBER 38. TELETYPE NUMBER 39. COUNTRY 40. COMMENTS	

SENSOR

The sensor operates on the principle of a fuel cell. The formaldehyde diffuses through a semipermeable membrane and undergoes electro-oxidation at a special sensing electrode. The resulting current is directly proportional to the partial pressure of the pollutant in the gas mixture. This current is amplified and the output of the amplifier is displayed on the meter. The selectivity of the sensor to formaldehyde is obtained by the unique membrane/electrolyte/electrode combination.

Each sensor is a sealed unit and no addition of any electrolyte is ever required. The sensor operating life may vary from 3 to 9 months depending upon the condition of the sample. Generally speaking, hot, dry and dirty samples will shorten the sensor life. The sensor may be conveniently replaced with a new sensor as described later. Drawings #672592 and 672021 show the design and specifications of the polypropylene transducer body.

SAMPLE CONDITIONING AND PRESSURE ADJUSTMENTS

The electrolyte used for the rapid, selective oxidation of formaldehyde imposes certain restrictions on the nature of the sample during automobile exhaust analysis. The gas stream should not contain more than 1% CO₂ and the relative humidity of the gas should not be higher than 50%.

The sensitivity of the AL-620 instrument has been increased to allow the sample to be diluted to meet these requirements. A standard procedure based on a tenfold dilution of the sample has proven to yield satisfactory results. Continuous exposure to automobile exhaust for periods longer than four hours may cause some drift in the calibration span.

The recommended method of analysis is exposure to the diluted sample gas for 30 minutes or less followed by flushing with a zero gas for 10 minutes. This procedure will guarantee trouble-free operation.

The formaldehyde ambient sensor AL-610 is designed for application in an environment characterized by a CO₂ content of 1000 ppm or less. It has a faster response time, lower sensitivity, and does not require sample dilution.

The following sampling requirements apply equally to both models. The temperature of the sample should be less than 100°F, preferably in the range 80-100°F. The conditioned sample can be passed over the sensor by connecting it to the input 1/4" polypropylene tube fitting provided it is at the right side when facing the back of the instrument. The sample passes through the sensor, flowmeter, and exits from the fitting on the left side which should be connected to the vent line. The instrument reading is independent of the flow rate. However, it is suggested that to get the optimum response time and a long operating life, a flow rate of 0.5 to 2.0 SCFH be kept steady throughout the run. If the flow indicator is kept in the blue area, the flow rate will be satisfactory.

The sample should be "pushed" rather than "pulled" through the sensor. However, if it is desirable to pull the sample by creating a suction at the exit, care must be taken to assure that the vacuum created in the sensor is not more than 3" of H₂O.

The sensor is designed for operation at atmospheric pressure. It can be operated "in line" at pressures slightly above or below atmospheric, but it is of utmost importance that any pressure changes occur slowly in order to prevent damage to the sensor.

Since the sensor measures the partial pressure of the gas being monitored, it must be realized that a correction should be made if the sensor has been calibrated at one pressure and is used at another. For example, calibration of the sensor at 740mm Hg of ambient atmospheric pressure and 10 ppm of CH₂O gas results in a full scale meter reading unique to 740mm Hg. If the total "in line" pressure is changed for example to 700mm Hg, and the ratio of molecules of CH₂O gas to total gas is kept constant at 10 ppm, then the new reading will be $\frac{700}{740}$ of full scale.

OUTPUT

The meter reading is directly proportional to the concentration of CH_2O . In addition, a 10 mV recorder output is provided in the back of the monitor for continuous recording. The output jack is available on the back of the instrument next to the sample outlet fitting.

POWER REQUIREMENTS

115/230 volts and 100 volts, 50 or 60 Hz powered from the three-prong receptacle on the back of the monitor. An optional 12 Vdc capability is available. The 12 Vdc input jack is provided on the back of the instrument next to the fuse.

HEATER

A heater assembly with the appropriate electronics is provided as a standard feature for the formaldehyde model. The purpose of the heater is to maintain a temperature environment for the sensor higher than 80°F , thereby improving the stability and accuracy of the system. At lower temperatures formaldehyde is absorbed by the surfaces in the sampling system.

When the outside temperature is below 80°F the heater must be utilized. The heater can be switched on by pushing the HEATER POWER switch on the front panel. About 3-1/2 to 4 hours are required for the sensor to come to equilibrium at a factory-set temperature of about 80°F .

To readjust the temperature set-point, proceed as follows:

- a.) Remove the printed circuit board from its receptacle.
- b.) Using an ohmmeter, check the resistance between Points A and B (see Drawing No. 602517, Printed Wiring Assembly) and adjust pot R41 to obtain 41K ohm resistance.
- c.) Install the printed circuit board back in its receptacle.

The heater is proportionally controlled thus eliminating the possible interference from an On/Off action. The HEATER red light on the front panel indicates the level of power to the heater. In the beginning when the HEATER POWER is switched on, the HEATER light is very bright. However, within the first two hours it starts dimming and stays fairly dim during the continuous operation.

CAUTION - If the HEATER light remains bright for more than two hours, turn the power off and check for possible malfunction in the heater circuit. The two white leads from the heater should be firmly plugged in the white jacks on the chassis which supply the power to the heater. Check the resistance across the two green leads after removing them from the chassis. These leads are joined to a thermistor which should read about 100 K ohm resistance at 77°F and about 45 K ohm resistance at the controlled temperature. A broken thermistor would show as infinite resistance and would keep the heater power on all the time.

CALIBRATION

The instrument may be calibrated in any RANGE position. However, for maximum accuracy, calibrate in the High Range. Turn on power to the instrument by pushing in the SYSTEM POWER switch. Set the RANGE switch to the desired position. Turn the SPAN knob completely clockwise. Wait about 15 minutes before proceeding with the calibration. If the heater is used, wait 4 hours before proceeding. Flow the zero gas (N_2 or formaldehyde free air) through the instrument and wait for 5 minutes. Then bring the reading to zero by adjusting the ZERO knob. Lock the ZERO knob. Pass the calibration gas over the sensor. Wait 5 minutes. Adjust the SPAN knob so that the meter reading corresponds to the concentration in the calibrated sample. Lock the SPAN knob.

The instrument is designed to be essentially drift-free ($\pm 1\%$ full scale per day) and will retain its calibration for a long time. However, for optimum results, calibrate the instrument at regular intervals.

SENSOR REPLACEMENT

The instrument is designed to be maintenance free. The sensor must never be taken apart. A fault in the sensor usually shows up as slower response time and/or inability to calibrate the instrument.

The faulty sensor may be easily replaced with a new sensor in the manner described below. The newly replaced sensor may take 6 to 8 hours to stabilize before it is ready for use. Before replacing the sensor, make sure that the slide switch located near the battery on the chassis is in the proper position. The use of models NR-210 and NR-230 requires the slide switch moved towards the front of the monitor. All other models require slide switch in the opposite direction as marked.

Installation of the AL-610 cell requires manual switching of the battery polarity using the switch located among the black cell jacks. The black cell-lead should be plugged into the terminal marked AL-610.

PROCEDURE FOR CHANGING SENSOR (UNITS WITH HEATER)

- Step 1: Disconnect 115V input power cord.
- Step 2: Remove (2) screws, item 65, and remove cover/rear panel assembly.
- Step 3: Disconnect (2) tube fittings, item 152.
- Step 4: Unplug electrical leads running from sensor to chassis.
- Step 5: Remove insulator, Item 130.
- Step 6: Remove (2) screws, Item 150, which hold cover, Item 141, to enclosure, Item 140.
- Step 7: Remove cover/sensor assembly 602580 and replace with new assembly.
- Step 8: Reverse Steps 1 through 7.

NOTE: Fittings, item 152, shall be firmly hand tightened only.

BATTERY CHECK

A size "D" mercury battery is used to bias the sensor. Its voltage at all times should remain $1.35 \text{ V} \pm 10\%$. The battery voltage may be checked by holding the RANGE switch on the front panel to the BATTERY TEST position. Replace the battery if the output on the meter shows less than 90% full scale deflection.

THE ELECTRONIC PACKAGE

During system operation the cell output current is converted to a proportional voltage by the Current Amplifier. This voltage signal is then scaled by the span control and amplified by the scaling amplifier. The scaling amplifier gain is determined by the range control (High - Med - Low) which provides a proper output for full scale meter deflection and recorder output.

DETAILED OPERATION

The current amplifier input is provided by the cell (MTI) and bias network composed of resistors R60 through R64, R68, R69 and battery (B). The function of the bias network is to provide the proper cell bias for system application required.

The front panel zero control circuit consists of pot R66, resistors R3, R4 and R5 and 6.2V zeners VR₁ and VR₂. This provides a $\pm$ current to offset residual cell currents.

Q₁, R₁ and R₂ are creating a short circuit to cell currents when the power is in the off state. This maintains the cell in a ready state for rapid stabilization.

The current amplifier is basically a low noise FET input amplifier which utilizes the $\mu\text{A } 741$ for high open loop gain and complementary output drivers Q₄ and Q₅ for linearity. Potentiometer R₁₃ and resistors R₁₀ and R₁₂ are used to zero the amplifier during initial alignment. The amplifier gain is determined by RT₁, R₁ and R₁₁. R₁ and R₁₁ are used to modify the temperature characteristic

of thermistor RT_1 . RT_1 and R_1 are physically located in the cell to obtain temperature tracking gain which will provide the best system accuracy during heater warm-up. The basic gain equation is:

$$V_o = I_{in} R_F$$

where V_o is the voltage at the emitters of Q_4 and Q_5 .

I_{in} is the cell current

$$R_F = R_{11} + \frac{R_1 RT_1}{R_1 + RT_1}$$

The scaling amplifier AR_2 is an inverting operational amplifier with four selectable gain settings determined by the range switch. The basic gain equation is:

$$A_v = \frac{R_f}{R_{in}}$$

where R_f is R_{19} for all ranges and R_{in} composed of one of the series resistors R_{17} , R_{18} or R_{44} and the equivalent source resistances. This source resistance is the effective resistance of the span pot R_{68} and any parallel resistance such as R_{16} or R_{45} .

To maintain an accurate meter reading, the meter is electrically contained in the feedback loop and the system is therefore immune to changes in the meter resistance as a function of time and temperature.

Overload protection for the circuit is provided by the diode network of CR_1 through CR_4 and R_{20} . This limits the amplifier to $\pm 1.4V$.

The recorder output is developed by the resistive divider R_{22} and R_{23} . This provides a 10 mV full scale output with a low output impedance.

Initial zero adjust for AR_2 is set by R_{21} . Temperature control of the cell heater is determined by resistive bridge amplifier AR_3 and associated driver transistors R_7 through R_9 .

The resistive bridge is composed of resistors R_{40} , R_{42} , R_{43} , RT_2 (thermistor) and potentiometer R_{41} . Bridge unbalance is sensed by amplifier AR_3 which

proportionally changes the output voltage to the heater. At 25°C the bridge unbalance causes pin 3 to be positive with respect to pin 2. The output at pin 6 is then at a maximum positive voltage. This voltage is buffered by emitter followers Q_7 and Q_8 which control the high current pass transistors Q_9 . As the heat increases, the thermistor RT_2 (located on the cell) will continue to decrease in value until the bridge becomes balanced. The high gain of the amplifier maintains the heater at a high input current for fast warm-up and then maintains a proportional control within a few tenths of a degree.

Circuit protection is obtained by the heater power switch S_2 and diodes CR_9 and CR_{14} .

The heater light $DS3$ is directly in parallel with the heater blankets and has a brilliance which is proportionate to the applied voltage.

Monitor power can be provided by either 115 VAC line voltage or +12 VDC. The +12 VDC operation is dependent on the PSI DC to DC converter. This is a special module which provides ± 22 V of partially filtered voltage in parallel with the rectified AC line voltage.

The filtered DC voltages are regulated by integrated circuit regulators Z_1 and Z_2 . The regulated ± 15 VDC is used to virtually eliminate the effects of line voltage and frequency. They also provide short circuit protection to prevent propagation failures. Initial adjustment is set by potentiometer R_{27} for the +15 VDC and R_{33} for the -15 VDC.

APPENDIX E

PARTS LIST

APPENDIX B

PARTS LIST

GENERAL

Appendix B contains a list of replaceable parts for the Dynasciences
Air Pollution Monitor.

To obtain replacement parts, address order of inquiry to:

Dynasciences Corporation
Instrument Systems Division
9601 Canoga Avenue
Chatsworth, California 91311

CARD NO.	SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	QUANTITY	CODE IDENT NO.	NEXT ASSY	SEGMENT NO.	REV
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	2			672051	ENCLOSURE	1				
		1		671919	PANEL, FRONT	1				
		2		672025	PANEL, REAR	1				
		3		*	SENSOR	1				
		4		672024	CHASSIS	1				
		5		672026	BRKT, FLOWMETER, MTG.	1				
		6		672039	SHIELD	1				
		7		IN4719	DIODE	1				
		8	CR13	672016	SWITCH, ROTARY	1				
		9	S3	602517	PRINTED WIRING BOARD ASSY	1				
		10		MODUC AW3-DMA-001-M-N-A19% ORANGE	METER	1				
		11		H.H. SMITH NO. 1227	SCALE 0-100	1				
		12	S4, S5	520-1017-11-392	SWITCH (SLIDE)	2		SEE CHASSIS DWG		
		13		MARCO-OAK	SWITCH/LIGHT	1				
		14		BURNS 35095-1-202	POTENTIOMETER 2K	1				
		15		BURNS 35095-1-103	POTENTIOMETER 10K	1				
		16		G.E. OR CHICAGO MINIATURE NO. 382	LAMP	1		REPLACEMENT LAMP FOR ITEM 12, 13, 14, 15		
		17		BURNS H 510-2	DIAL, TURNS COUNT	2				
		18								
		19		MS91528-1P2B	KNOB	1				
		20		H.M. SMITH 1415-A	TERMINAL LOG, LOG	1				
		21		SWITCHCRAFT AC22	SOCKET, 115V	1				

ENGINEERING	CORPORATION	CHASSIS	CHASSIS	CHASSIS
		CHASSIS	CHASSIS	CHASSIS
CODE IDENT NO.		06692	PL 631035	
SHEET		2	REV	

CARD NO.	SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	QUANTITY	CODE IDENT NO.	NEXT ASSY	SEGMENT	PUN REV NO.
1	2	3	4	5	6	7	8	9	10	11
			(8)	(15)	(15)	(13)	(6)	(13)	(4)	(12)
						44	3139	5071		620736
		22		672360	CLAMP, SENSOR	1	USED WITH SENSOR (MODULE 400) ONLY			
		23		BUSSMAN HMB	FUSEHOLDER	1				
		24		BUSSMAN 3AG 2A, 50-PC2M	FUSE	1				
		25		AMPHENOL 80-PC2M	CONNECTOR, RECEPTACLE	1				
		26		AN743Z1Z	BRACKET, SUPPORT	1	USED WITH SENSOR (MODULE 400) ONLY			
		27		AMPHENOL 80-PC2F	CONNECTOR, RECEPTACLE	1				
		28								
		29		SWITCHCRAFT XC-1351-3	CABLE ASSEMBLY	1				
		30								
		31		CALABRO PLASTICS, INC. UNITRACK PAD4125	GUIDE, CARD	2				
		32								
		33		CALABRO PLASTICS, INC. VERSAMOUNT	BRKT, CARD GUIDE	2				
		34								
		35		AVATON 8213-B-0440-3A	STAND-OFF 3/8" LG	4				
		36		AVATON 8102-B-0440-3A	STAND-OFF 1/4" LG	4	NOT PRESENTLY USED			
		37		AVATON 8397-A-1032-3A	STAND-OFF 3/4" LG	4				
		38		AMPHENOL M3-036-01	CONNECTOR	1				
		39		CAMBIUM 2870-01-02	BRKT, BATTERY MOUNT	1				
		40								
		41		ELDEN 1725B-5, 8FT No. 18-3, TYPE 5, VT	CORD, POWER	1				
		42								
		43		672079	X FORMER	1				
ENGINEERING					CHATSORTH CALIFORNIA	CODE IDENT NO.		PL631035		
PARTS LIST					CORPORATION	06692		SHEET 3		

CARD NO.	SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	QUANTITY	CODE IDENT NO.	NEXT ASSY	SEGMENT	RUN REV
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
1	2					39 30	44 45	47 48	51 52	57 58
		44		MALLORY DURA-CELL RM-42R 1.35V MERCURY	BATTERY	1				
		45		BISHOP IND'S T207 BLUE	TAPE, .156 WIDE	AR				
		46		HARRINGTON PLASTICS P-61005	UNION, BULK-HEAD	2				
		47		HARRINGTON PLASTICS P-61005	ELBOW	2				
		48		RUSSELL IND'S NO.602-2252	GROMMET	2				
		49			SCREW, 7 RECESSED PAN HD CD PL 10-32 X 3/8 LG	4				
		50		HARRINGTON PLASTICS 1/4" OD	TUBING	4 FT				
		51		8-32 X 3/8 LG	SCREW, 7 RECESSED PAN HD CD PL 10-32 X 3/8 LG	2				
		52		8-32	SCREW, 7 RECESSED PAN HD CD PL 10-32 X 3/8 LG	3				
		53		STAKE FASTENER CO SFS4050-SOI BN	SCREW, 7 RECESSED PAN HD CD PL 10-32 X 3/8 LG	8				
		54		STAKE FASTENER CO SFS6060-SOI BN	SCREW, 7 RECESSED PAN HD CD PL 10-32 X 3/8 LG	4				
		55		NO. 8	WASHER, FLAT	3				
		56		SCIENTIFIC ATLANTA OPTIMA HW-35	6-32 TINNERMAN NUT	5				
		57			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	2				
		58			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	6				
		59			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	12				
		60			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	2				
		61			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	2				
		62			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	4				
		63			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	4				
		64			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	2				
		65			SCREW, 7 RECESSED PAN HD, CD PL 10-32 X 3/8 LG	13				

ENGINEERING CORPORATION	CHATS WORTH CALIFORNIA	CODE IDENT NO. 06692	PL 631035	SHEET 7	REV D
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CARD SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NAME OR DESCRIPTION	QUANTITY	CODE IDENT. NO.	NEAT ASSY	SECURITY NO.	REV
1	2	(8)	(15)	(16)	13	(6)	(13)	(4)	(12)
	66			WASHER, SPLIT, CD PL, NO. 2	6				
	67			WASHER, SPLIT, CD PL, NO. 4	25				
	68		WADONOR, HARDWARE (REF NEWARK NO. 318167)	WASHER, FELT, FERR. JOLIX. 3750D X. 02 THK	9				
	69			NUT, HEX, CD PL, 4-40	12				
	70			WASHER, SPLIT, CD PL, NO. 10	10				
	71			WASHER, FELT, FERR. 00 CD PL, NO. 6, 1/32 THK.	4				
	72		3006714	NUT, PLATE	1				
	73		HACONSTEN PLASTIC	1/2" DIA. POLYETHYLENE TUB	6 IN				
	74		CTC 4887-1-05-16	TERMINAL, INSULATED	10				
	75								
	76		672165-1	BUTTON, PLUG, 3/32 O.D.	1				
	77		672165-2	BUTTON, PLUG, 5/8 O.D.	1				
	78		E.F. JOHNSON 105-603 (BLACK)	TIP JACK	8				
	79		E.F. JOHNSON 105-602 (RED)	TIP JACK	1				
	80		E.F. JOHNSON 105-607 (YELLOW)	TIP JACK	2				
	81		E.F. JOHNSON 105-604 (GREEN)	TIP JACK	2				
	82		E.F. JOHNSON 105-601 (WHITE)	TIP JACK	2				
	83		~~E.F. JOHNSON 105-602 (BLUE)~~	~~TIP JACK~~	1				
	84			NUT, HEX, CD. PL. NO. 2-56	4				
	85		# 8	WASHER, LOCK HEL. CAP PLATE	2				
	86		# 8-32 X 1/2 LG	SCREW, PAN HEAD, 8-32 X 1/2 LG	1				

DELETE ONLY UNITS
EQUIPPED WITH HEATER

ENGINEERING		CODE IDENT. NO.		PL 631035	
PARTS LIST		06692		SHEET 5	
CORPORATION		CHATSWORTH CALIFORNIA		REV	

CARD NO.	SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	QUANTITY	CODE IDENT NO.	NEXT ASSY	SEGMENT	RUN NO.	REV
1	2	(3)	(8)	(15)	(15)	ASSY	SYST	(13)	(4)	(2)	(2)
		87	C22	GEN INST DM19FD272J03	CAPACITOR, 500V CAPACITOR, 2700PF	1	3152	3758	(4)	74	75
		88		974-130G (GENERAL INST.)	CAPACITOR, 100UF, 25V	1	USED W/O HEATER OPTION				
		89	CR11, CR12	IN4816	DIODE	2					
		90		AMP NO. 34149	TERMINAL	2					
		91	R60	RN55C93R1B	RESISTOR, 93.1±.1%, 1/4W	1					
		92	R61	RN55C37R4B	RESISTOR, 37.4±.1%, 1/4W	1					
		93	R62	RN55C1690B	RESISTOR, 169±.1%, 1/4W	1					
		94	R63	RN55C56R2B	RESISTOR, 56.2±.1%, 1/4W	1					
		95	R64		RESISTOR, 100±5%, 1/4W	1					
		96	R67	RN60E1371F	RESISTOR, 1.37K, ±1%, 1/4W	1					
		97	E8,E9	USECO 1471B	TERMINAL	2		MOUNTED ON ROTARY SWITCH			
		98		SK INST. PURGE ROTOMETER NO. 207010, VITRON A "O" RINGS, TUBE SIZE, E132-08-P- 1 1/2, FLOAT NO. SP-5 SCALE 0-10, FLOW RANGE 0-1.0 SCFH	FLOWMETER	1		MOUNTED ON ROTARY SWITCH			
		99	R68		RESISTOR, CARBON R. 9.9, ±5%, 1/4W	1					
		100	R69	RN55C37R4B	RESISTOR, 37.4±.1%, 1/4W	1					

ENGINEERING PARTS LIST

DYNASCIENCES
CORPORATION
INSTRUMENT SYSTEMS DIVISION
A DIVISION OF VV CORPORATION
CHATSWORTH
CALIFORNIA

CODE IDENT NO
06692

PL 631035
SHEET 6
REV

CARD NO.	SYSTEM NO.	ITEM NO.	REFERENCE DESIGNATOR	PART OR IDENTIFYING NUMBER	NOMENCLATURE OR DESCRIPTION	QUANTITY ASSY	QUANTITY SST	CODE IDENT NO.	NEXT ASSY	SEGMENT	RUN NO.	REV LTR
(1)	(2)	(3)	(8)	(15)	(16)	(7)	(9)	(6)	(10)	(4)	(5)	(3)
					PART REQD FOR 12VDC OPTION ONLY							
		99		672164	CABLE ASSY	1		06692				
		100		COMPUTER LOGIC CORP DP SERIES K/DC/21/25 TURRET TERMINALS	POWER SUPPLY	1						
		101			SCREW, X RECESSED PAN HD, CD PL, 4-40X1/4LG	2						
		102			WASHER, SPLIT, CD PL NO. 4	2						
		103		672032	BRKT, POWER SUP MTG	1						
		104			SCREW, X RECESSED PAN HD, CD PL, 6-32 X1/4LG	2						
		105			WASHER, SPLIT, CD PL NO. 6	2						
		106			NUT, HEX, CD PL, NO. 6	2						
		107										
		108										
		109										
		110										
		111										
		112										
		113										
		114										
		115										
		116										
		117										

PL 631035
SHEET 7
REV B

[illegible]



6. ADJUST R41 TO CHANGE RESISTANCE BETWEEN A8B
FOR ALTERNATE HEATER SET POINT.
5. EXPOSE ITS 168 TO BOARD WITH EASTMAN 9.0.
4. SOLDER PER DWG NO. 690143.
3. COMPONENTS RT1 THRU RT4 & R46 MAY NOT BE USED.
2. REFERENCE DESIGNATIONS ARE SHOWN FOR REFERENCE ONLY
AND DO NOT APPEAR ON COMPONENT PARTS OR BOARD.
1. FOR SCHEMATIC SEE DWG NO. 660748.
- NOTES: UNLESS OTHERWISE SPECIFIED

4

1

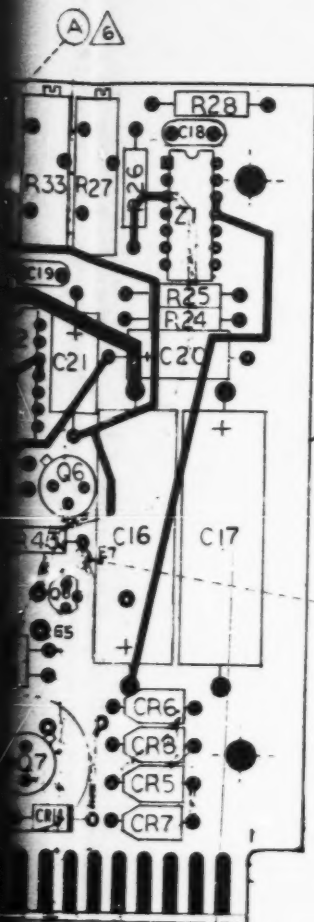
3

2

1

REL CLASS	DISTR CODE	ZONE	LTR	DESCRIPTION	DATE	APPROVED
Prod	8					
		A		SEE DCN 24 SEP 70 E.M.H.	7-2-70	89

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FOR PARTS LIST SEE PL602517

DASH NO.		BASIC ZONE	PART NUMBER	CODE IDENT	DESCRIPTION	REFERENCE DESIGNATOR	ITEM NO.
REQD PER ASSY		- PARTS LIST					
UNLESS OTHERWISE SPECIFIED INTR DWG PER MIL-STD-100 DIM. ARE IN INCHES DO NOT SCALE DRAWING DIM. TO BE MET AFTER FINISH STANDARD HOLES PER ANSI 10.1 SURFACE ROUGHNESS $\sqrt{\text{ }}$		MATERIAL		CONTRACT NO.		DYNASCIENCES CORPORATION INSTRUMENT SYSTEMS DIVISION CHATSWORTH, CALIFORNIA	
CUSTOMER & SPEC		HEAT TREAT		DRAWN BY J. K. K... CHECKED DESIGNER DATE 5-26-70		TITLE PRINTED WIRING ASSY NOX MONITOR	
SIMILAR TO		FINISH		APPROVED H.W. 6-29-70 W. K...		SIZE D 06692	
		NEXT ASSY MULTI		USED ON MULTI		DWG NO. 602517	
						SCALE 2/1 WT SHEET	

NOX BOX

-90-

D

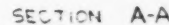
C

B

A 602517

A

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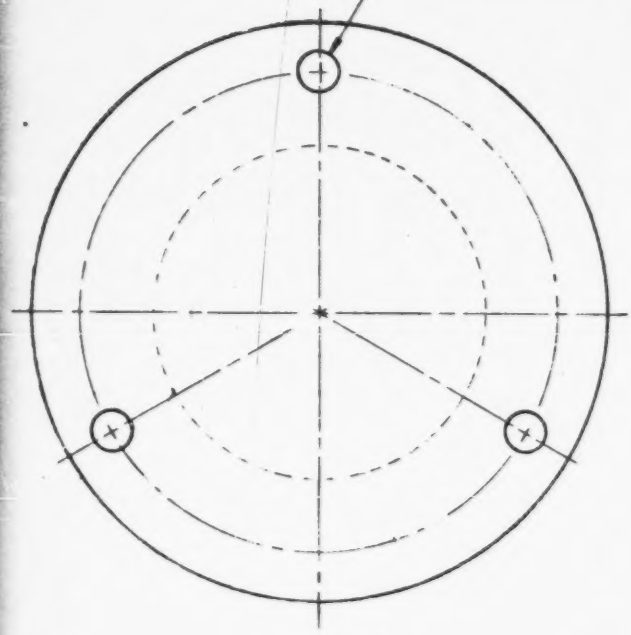
- 1 MAY BE PURCHASED FROM CADILLAC PLASTICS & CHEM.CO.
2305 W BEVERLY BLVD, L.A, CALIF.

240 INTERNATIONAL JOURNAL OF ENVIRONMENT & DEVELOPMENT

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REL CLASS	DISTR CODE	ZONE	LTR	DESCRIPTION	DATE	APPROVED
	8					
		A		REPLACES REV "NC" WITH CHANGE. SEE DCN 8 AUG 70	10-7-70	AM
		B		SEE DCN	10-7-70	MC

.242^{+.003}_{-.001} DIA X .376^{+.010}_{-.000}
FLAT BOTTOM
3 HOLES EQ SP ON
A 2.875 B.C.



REAR VIEW

THRU
-2B
IN THD LG
35 DIA X 17 DF

2		6	1185-3CN		INSERT, HELICOIL		2	
		1	-1	06692	BODY		1	
	DASH NO.	BASIC	ZONE	PART NUMBER	CODE IDENT	DESCRIPTION	REFERENCE DESIGNATOR	ITEM NO.
	REQD PER ASSY				PARTS LIST			

UNLESS OTHERWISE SPECIFIED INTR DWG PER MIL-STD-100 DIM ARE IN INCHES DO NOT SCALE DRAWING DIM. TO BE MET AFTER FINISH STANDARD HOLES PER ANSI B91.3 TOL $\pm .010$ $\pm .005$ SURFACE ROUGHNESS TOL $\pm .010$ $\pm .005$ CUSTOMER & SPEC		MATERIAL POLYPROPYLENE ROD, COLOR: NATURAL HEAT TREAT FINISH NONE NEXT ASSY 620413		CONTRACT NO. DRAWN BY CHECKER DESIGNER APPROVED HRW 7-15-70		DYNASCIENCES CORPORATION INSTRUMENT SYSTEMS DIVISION CHATSWORTH CALIFORNIA TITLE BODY ELEC/CHEM SENSOR SIZE D 06692 SCALE 2/1 WT		DWG NO. 672021 SHEET	
---	--	---	--	--	--	--	--	----------------------------	--

41-

NOX BOX

D
C
B
F 672021

8

7

6

5

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$\pm .006$
 $-.001$
339 DIA THRU
1/8 - 27 NPT 2 PLACES

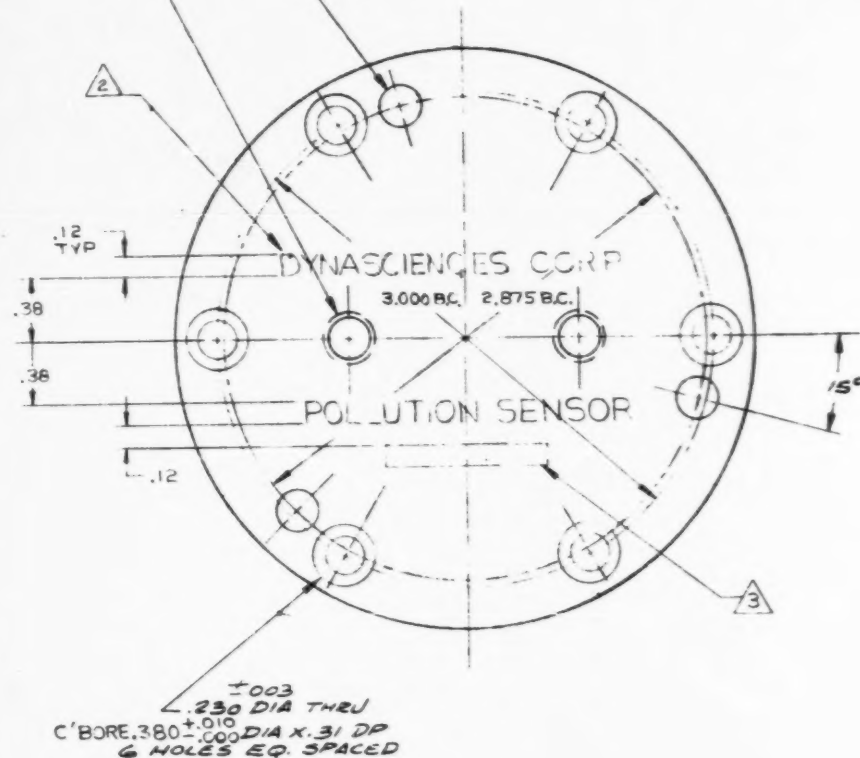
$-.003$
 $-.001$
 $\pm .010$ DP
242 DIA X .376
FLAT BOTTOM 3 HOLES
EQ. SPACED Δ

$\pm .005$ DIA
 $-.001$
2.00 $\pm .03$ DP

D

C

B



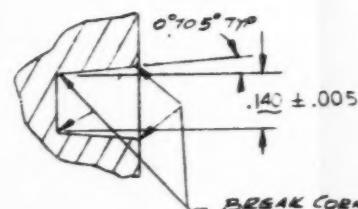
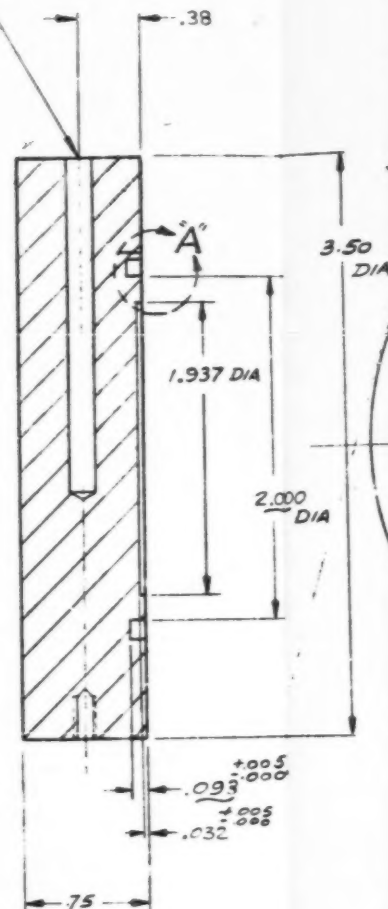
Δ 3 VENDOR TO ENGRAVE SERIAL NUMBER AS INDICATED BY PURCHASE ORDER.

Δ 2 ENGRAVE STD GOTHIC CHARACTERS .005 TO .010 DEEP AND FILL WITH DULL BLACK ACID RESISTANT PAINT, CENTER ON COVER CENTER LINE, AS SHOWN.

Δ 1 MAY BE PURCH. FROM: CADILLAC PLASTIC & CHEM. CO. 2305 W. BEVERLY BLVD. L.A. 57 CALIF.

NOTES: UNLESS OTHERWISE SPECIFIED

11-10 DYNASCENCES CLEARPRINT 100-10



DETAIL "A"
SCALE NONE
FINISH ALL INSIDE SURFACES

4

3

2

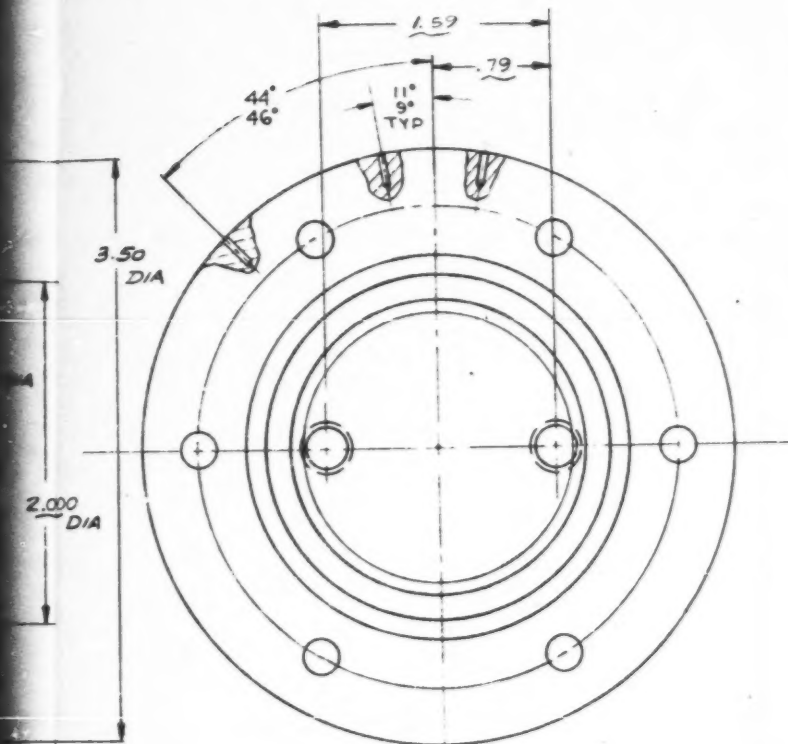
1

REL CLASS	DISTR CODE
PROP	5

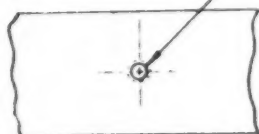
REVISIONS

ZONE	LTR	DESCRIPTION	DATE	APPROVED

.054^{+.004}_{-.001} DIA
.137^{±.010} DP
3 HOLES



6-32 UNC-2R THD
.25 DP



±.005

ALL CORNERS APPROX .005

DASH NO.	BASIC	ZONE	PART NUMBER	CODE IDENT	DESCRIPTION	REFERENCE DESIGNATOR	ITEM NO.

REQD PER ASSY

PARTS LIST

UNLESS OTHERWISE SPECIFIED
INTR DWG PER MIL-STD-100
DIM. ARE IN INCHES
DO NOT SCALE DRAWING
DIM. TO BE MET AFTER FINISH
STANDARD HOLES PER ANSI B91
SURFACE ROUGHNESS
RA = .010 MAX ± .005

CUSTOMER & SPEC

SIMILAR TO

MATERIAL
POLYPROPYLENE
COLOR NATURAL

HEAT TREAT

FINISH

NEXT ASSY

USER ON

CONTRACT NO.

DRAWN BY

CHECKER

DESIGNER

MUCH APPR

ELEC APPR

APPROVED

DATE

MATERIAL

FINISH

MUCH APPR

ELEC APPR

APPROVED

DYNASCIENTES
CORPORATION

INSTRUMENT SYSTEMS DIVISION
A DIVISION OF WESTERN ELECTRIC

CHATSORTH
CALIFORNIA

TITLE

COVER,
ELEC/CHEM. SENSOR

SIZE

D 06692

CODE IDENT NO.

DWG NO.

672 952

SCALE 1/4" = 1" WT

SHEET

NOX BOX

42

D

C

B

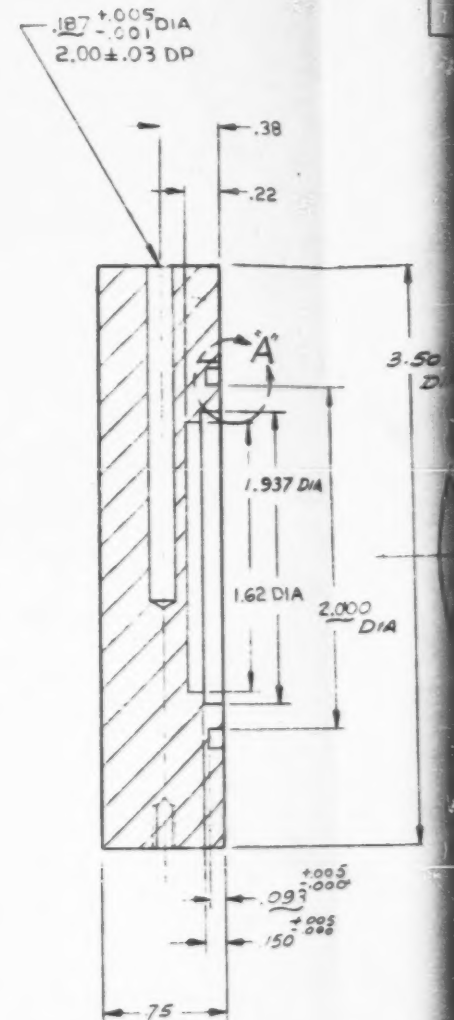
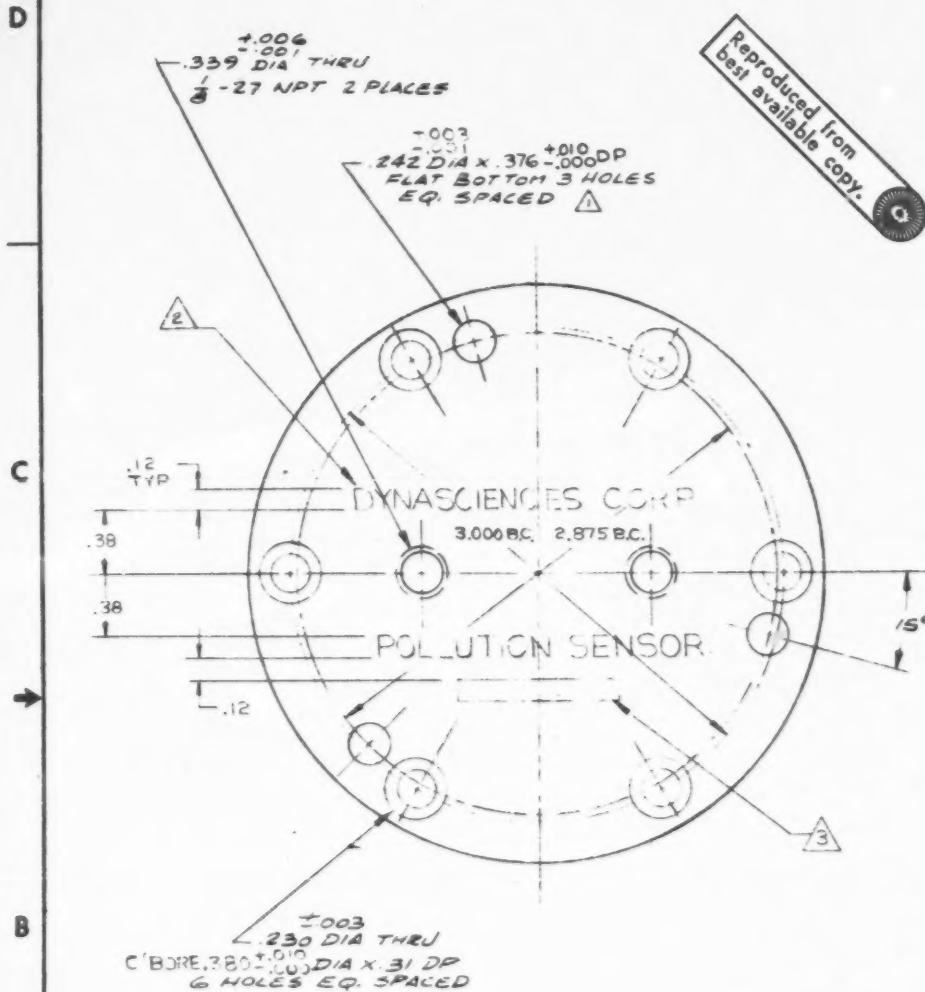
E672952

A

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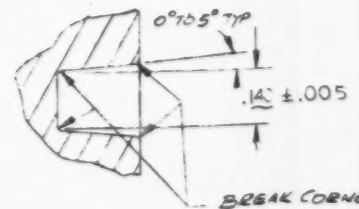
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- Δ VENDOR TO ENGRAVE SERIAL NUMBER AS INDICATED BY PURCHASE ORDER.
- Δ ENGRAVE STD GOTHIC CHARACTERS .005 TO .010 DEEP AND FILL WITH DULL BLACK ACID RESISTANT PAINT, CENTER ON COVER CENTER LINE, AS SHOWN.
- Δ MAY BE PURCH. FROM: CADILLAC PLASTIC & CHSM. Co. 2305 W. BEVERLY BLVD. L.A. 57 CALIF.

NOTES: UNLESS OTHERWISE SPECIFIED



DETAIL 'A'
SCALE NONE
63/ FINISH ALL INSIDE SURFACES

4

3

2

1

REL CLASS	DISTR CODE
PROD	0

ZONE

LTR

A

SEE DCN

E-4441

26 AUG 70

DATE

APPROVED

28 AUG 70

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

J. H. H.

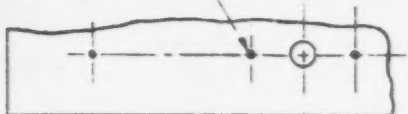
J. H. H.

J. H. H.

J. H. H.

J. H. H.

.054^{+0.004}_{-.001} DIA
.197^{±.010} DP
3 HOLES

44°
46°11°
9°
TYP

1.37

.68

3.50
DIA2.00
DIA

6-32 UNC-2R THD
.25 DP



.005

CORNERS APPROX. .005

DASH NO.	BASIC	ZONE	PART NUMBER	CODE IDENT	DESCRIPTION	REFERENCE DESIGNATOR	ITEM NO.
REQD PER ASSY							
PARTS LIST							
CONTRACT NO.				DYNASCENCES CORPORATION			
DRAWN BY		DATE		INSTRUMENT SYSTEMS DIVISION			
CHECKED		JUL 70		CHATSWORTH CALIFORNIA			
DESIGNER		JUL 70		TITLE			
MECH APPR		JUL 70		COVER			
ELEC APPR		JUL 70		ELEC/CHEM. SENSOR			
APPROVED		JUL 70		SIZE			
HRLW 7-16-70		JUL 70		CODE IDENT NO.			
				D 06692			
				DWG NO.			
				672020			
				SCALE			
				3/4" = 1" WT			
				SHEET			
				NOX FOX			

UNLESS OTHERWISE SPECIFIED INTR DWG PER MIL STD-100 DIM ARE IN INCHES DO NOT SCALE DRAWING DIM-TO BE MET AFTER FINISH STANDARD HOLES PER ANSI B1.1	
SURFACE ROUGHNESS XX = ±.010 XXX = ±.005	
CUSTOMER & SPEC	
SIMILAR TO	
MATERIAL POLYPROPYLENE COLOR NATURAL	
HEAT TREAT	
FINISH	
NEXT ASSY 620470 620480	
USED ON MULTI	

D

C

↑

B

A

A

B

A

B